SYNTHESIS, CHARACTERIZATION, AND PROPERTIES EVALUATION OF VALUE-ADDED POLYMER MATERIALS FROM GLYCEROL: POLYGLYCEROL, HYDROGELS AND OIL-GELS

Carolina Ardila Suárez

UNIVERSIDAD INDUSTRIAL DE SANTANDER

FACULTAD DE INGENIERÍAS FISICOQUÍMICAS

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Carolina Ardila Suárez, Ing.

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Directores:

Álvaro Ramírez García, Ph.D.

Gustavo Emilio Ramírez Caballero, Ph.D.

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Dedicatoria

Gloria a Dios. Dedicado con todo mi corazón a mis padres, Armando y Yolanda y a mi esposo e hijo Oscar Iván y Nicolás. El apoyo de ustedes, mi familia, ha sido incondicional. Sinceros agradecimientos desde lo más profundo de mi ser por apoyarme siempre en la consecución de mis metas. Los amo profundamente.

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Autor: Carolina Ardila Suárez**

Palabras Clave: Glicerol, poliglicerol, hidrogeles, absorbentes de solventes no polares.

En este trabajo de investigación, se estudió el efecto de las condiciones de síntesis en la morfología y propiedades térmicas de poligliceroles sintetizados directamente a partir del glicerol, un monómero biodegradable. La sincronización de las condiciones de síntesis con las propiedades finales del poliglicerol, le abre las puertas a este polímero para aplicaciones antes limitadas únicamente a poligliceroles derivados de monómeros tóxicos. Por otro lado, se estudió la cinética de la reacción de polimerización del glicerol para la síntesis de poliglicerol mediante la técnica de análisis termogravimétrico. Asimismo, se estableció el efecto de las impurezas del glicerol crudo la síntesis de poliglicerol; se encontró que de las impurezas del glicerol crudo, los jabones son el cuello de botella para la obtención del polímero. Adicionalmente, se emplearon ácidos biodegradables tales como el ácido cítrico y el ácido oleico como agentes modificantes de la estructura del poliglicerol con el fin de obtener materiales poliméricos de alto valor agregado, los cuales fueron sintetizados, caracterizados y evaluados con éxito. El poliglicerol fue el polímero base para la síntesis de redes poliméricas para la formación, por ejemplo, de hidrogeles los cuales presentaron variaciones en su comportamiento de absorción de agua ante estímulos externos de temperatura y pH. Además el poliglicerol fue el material base para la síntesis de absorbentes de solventes no polares, los cuales fueron caracterizados mediante pruebas de absorción en tolueno y en soluciones de crudos livianos y pesados en tolueno. Los anteriores materiales podrían tener un impacto relevante en aplicaciones industriales.

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* Trabajo de Investigación de Maestría en Ingeniería: Área Ingeniería Química

** Facultad de Ingenierías Físico-Químicas, Escuela de Ingeniería Química. Director: Álvaro Ramírez García, Ph.D. Director: Gustavo Emilio Ramírez Caballero, Ph,D.

ABSTRACT

TITLE: SYNTHESIS, CHARACTERIZATION, AND PROPERTIES EVALUATION OF VALUE-ADDED POLYMER MATERIALS FROM GLYCEROL: POLYGLYCEROL, HYDROGELS AND OIL-GELS*

Author: Carolina Ardila Suárez**

Keywords: Glicerol, poliglicerol, hidrogeles, absorbentes de solventes no polares.

In this research study, the effect of synthesis conditions of polyglycerol –derived directly from glycerol, a biodegradable monomer- on morphology and thermal properties was studied. The tune of the synthesis conditions with final properties of polyglycerol opens possibilities to this polymer for applications once limited only to polyglycerol derivatives from toxic monomers. Furthermore, the kinetics of the polymerization of glycerol reaction to the formation of polyglycerol was studied by thermogravimetric analysis technique. Also, the effect of the impurities of the crude glycerol in polyglycerol synthesis was established; It was found that of the crude glycerol impurities, soaps content was the bottleneck to obtaining polymer. Additionally, biodegradable acids such as citric acid and oleic acid as modifying agent of polyglycerol structure in order to obtain polymeric materials with high value added, which were successfully synthesized, characterized and evaluated. Polyglycerol was the building block polymer for the synthesis of polymer networks to form, for example, hydrogels which possess variations on water absorption behavior to external stimuli of temperature and pH. Likewise, polyglycerol was the base material for the synthesis of oil gels, which were characterized by absorption tests in toluene and also, in solutions of light and heavy oils in toluene. The above materials could have a significant impact on industrial applications.

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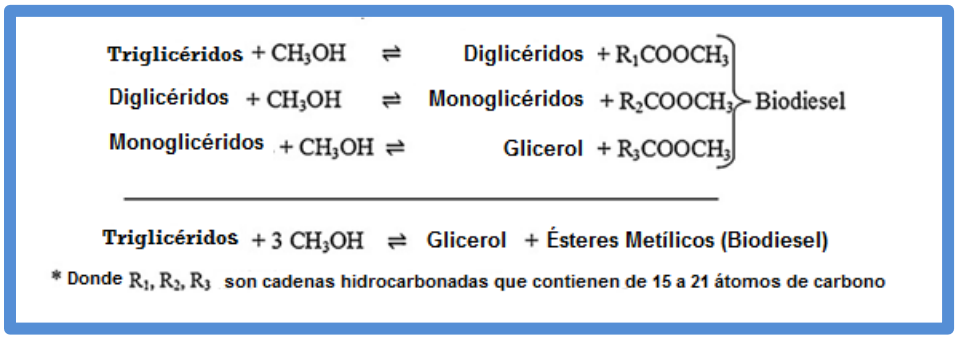
INTRODUCCIÓN

El uso de biomasa como fuente de energía alternativa a la energía producida por los combustibles derivados del petróleo, ha sido fuertemente impulsada por políticas gubernamentales a nivel mundial [1-3]. Las principales motivaciones han surgido como respuesta a preocupaciones ambientales por las emisiones de gases de efecto invernadero debido a la combustión de los hidrocarburos derivados del petróleo [4-6], la seguridad energética, amenazada por los constantes aumentos del precio del petróleo, y la inestabilidad geopolítica de los países con grandes reservas [7].

La utilización de biomasa como materia prima para la producción de combustibles es una fuente alternativa atractiva [8, 9], además de ser una fuerza impulsora para el desarrollo de biorrefinerías [10-12]. En este contexto, el biodiesel proveniente de aceites vegetales se ha consolidado como una alternativa con alto potencial para el remplazo del diesel convencional [13]. En la transesterificación de aceites vegetales catalizada por bases, generalmente hidróxidos de sodio o potasio, se lleva a cabo la hidrolisis de los triglicéridos donde se liberan moléculas de glicerol, como el mayor co-producto de la reacción y la formación de ésteres metílicos como producto principal [14].

En la estequiometria de la reacción de transesterificación de aceite vegetal, tres moles de metanol reaccionan, en tres etapas, con los glicéridos en presencia de catalizador para producir ésteres metílicos y glicerol. En la primera etapa, el metanol reacciona con los triglicéridos para formar diglicéridos y ésteres metílicos. En la segunda etapa, el metanol reacciona de nuevo, esta vez con los diglicéridos para formar monoglicéridos y ésteres metílicos. Finalmente en la tercera etapa, los monoglicéridos reaccionan con el metanol para formar glicerol y ésteres metílicos (Gráfica 1). De acuerdo con las reacciones descritas anteriormente, un mol de glicerol es producido por cada 3 moles de ésteres metílicos sintetizados. La

producción de glicerol respecto a la formación de ésteres metílicos equivale aproximadamente al 10% en peso [15].



Gráfica 1 Formación del glicerol crudo durante el proceso de transesterificación**.** [**15**]

La producción de glicerol crudo está aumentando exponencialmente como consecuencia del incremento en la producción mundial de biodiesel y se proyecta que puede alcanzar una cifra de 1,54 millones de toneladas en 2015 [16]. La sobreoferta de glicerol tiene efectos negativos sobre el medio ambiente [17] y sobre la rentabilidad del proceso de producción de biodiesel si no se aprovecha adecuadamente. Por lo tanto, la obtención de productos de alto valor agregado a partir del glicerol, contribuye a la sostenibilidad y mayor rentabilidad para la industria del biodiesel, así como también en beneficio ambiental [15, 18].

Actualmente, el glicerol que se utiliza en aplicaciones industriales requiere, al menos, de un nivel de pureza del 85%. El proceso de purificación para llevar el glicerol crudo a dicho nivel de pureza, representa aproximadamente un 14% del costo total de producción [17]. Los elevados costos de purificación del glicerol crudo para obtener glicerol purificado, se deben al requerimiento de técnicas de separación, electroquímicas [19], de intercambio iónico [20] y de destilación al vacío [21], las cuales implican altos costos de energía y de operación. Dentro de las impurezas a remover se encuentran residuos de catalizador y alcohol, ácidos grasos libres, ésteres alquílicos, mono, di y triglicéridos [22].

Los campos de aplicación del glicerol, siendo este un compuesto muy versátil [23], se encuentran principalmente en la producción de materiales con

aplicaciones en industria química básica, microbiología industrial y aditivos oxigenados para combustibles tales como, carbonato de glicerol [24, 25]; acroleína [26, 27] y 1,2 propanodiol [28, 29]. Adicionalmente, el glicerol puro tiene aplicaciones en la industria de alimentos, microbiología industrial, farmacología y cosmética; sin embargo, estas requieren de un nivel de pureza mayor al 99%, lo cual implica intensa labor de purificación [15]. Por el contrario, la utilización del glicerol crudo como materia prima para el desarrollo de productos para aplicaciones industriales, no demandaría costos de purificación para ser empleado como materia prima. Por esta razón, actualmente, se están haciendo investigaciones enfocadas en la búsqueda de un valor agregado del glicerol crudo que le permita ser utilizado en aplicaciones industriales que incluyen la producción de hidrógeno [30-32], producción de polihidroxialcanoatos (PHAs) [33-36], como poliol en la producción de espumas de poliuretanos [37, 38], y producción de biogás [39, 40], con el fin de transformar la industria del biodiesel actual, en una biorrefinería con base en la industria oleoquímica [41].

Una de las formas de darle valor agregado al glicerol, es polimerizarlo. El poliglicerol es un polímero conformado por una estructura central inerte de poliéter y un número abundante de grupos hidroxilos altamente reactivos, que se encuentran expuestos y que permiten su modificación para la producción de una variedad de compuestos derivados [42-44]. La reacción de polimerización del glicerol que da origen al poliglicerol requiere de la presencia de catalizadores de tipo homogéneos o heterogéneos, los cuales a su vez, pueden ser ácidos o básicos. La reacción directa de glicerol analítico a poliglicerol en presencia de catalizadores heterogéneos, tales como sólidos mesoporosos de la familia MCM-41, presenta ventajas como la fácil remoción y alta selectividad. Sin embargo, exhibe niveles bajos de conversión, y como consecuencia, se obtienen productos de bajo peso molecular [45, 46]. En cuanto a catalizadores homogéneos, se ha encontrado que con respecto a catalizadores básicos, los carbonatos tienen mayor actividad que los hidróxidos en la reacción de polimerización debido a una mejor

solubilidad en la masa reaccionante a altas temperaturas [47]; las reacciones de eterificación ácida homogénea del glicerol, producen poligliceroles con alto grado de polimerización. Sin embargo, no son reacciones selectivas y por consiguiente, ocurren reacciones de deshidratación y oxidación que causan una coloración en los productos finales [48]. Salehpour y Dubé [49] evaluaron el ácido sulfúrico como catalizador en la reacción de polimerización del glicerol a presiones reducidas y obtuvo poligliceroles de relativo alto peso molecular. En cuanto a la utilización del glicerol crudo como monómero de la polimerización, Ahmad [50], utilizó los jabones residuos del proceso de transesterificación como catalizadores de la reacción, obteniéndose oligómeros de glicerol.

El poliglicerol es industrialmente producido mediante polimerización del glicidol, vía apertura de anillo (*ring – opening polymerization*), de la cual se obtienen polímeros de estrecha distribución y pesos moleculares en un intervalo entre 1000 a 30000 g/mol [42, 51-53]. Los poligliceroles de alto peso molecular y de estructura ramificada sintetizados directamente del glicerol, podrían remplazar a los polímeros hiperramificados obtenidos a partir del glicidol, monómero tóxico [54], abriendo las posibilidades de aplicación a nivel industrial para la producción de estructuras poliméricas complejas, ya sean hidrofílicas, anfifílicas e incluso hidrofóbicas. Las reacciones de esterificación para la modificación de poligliceroles hiperramificados han sido estudiadas para la obtención de estructuras anfifílicas. La esterificación simple de poligliceroles ramificados (sintetizados a partir de derivados del glicerol) con ácidos grasos ofrece potenciales estructuras núcleo – caparazón anfifílicas con aplicaciones en biotecnología [55] y extracción de impurezas solubles en agua, dentro de un medio no polar [56]. Además, como los ésteres de poliglicerol pueden presentar diferentes comportamientos que van desde un carácter hidrofílico hasta uno completamente hidrofóbico, de acuerdo al grado de esterificación de sus grupos hidroxilos, son estructuras adecuadas para el diseño y síntesis de complejos poliméricos entrecruzados, como los hidrogeles y los materiales absorbentes de solventes no polares. La capacidad de absorción

de estos materiales poliméricos absorbentes se debe a la presencia de volúmenes libres dentro de la estructura del material, los cuales se forman por el entrecuzamiento de las cadenas poliméricas ramificadas que no permiten su disolución en solventes afines

Los hidrogeles son estructuras tridimensionales entrecruzadas de polímeros hidrofílicos que pueden absorber y retener cantidades significativas de agua [57, 58]. Los grupos funcionales presentes en la estructura de los hidrogeles afines a solventes polares, son los causantes de su hinchamiento y a su vez, permiten alterar sus propiedades en respuesta a estímulos del ambiente como pH, temperatura, luz, concentración iónica, campos eléctricos y magnéticos [59-61]. Debido a su capacidad de retención de agua y respuesta a estímulos ambientales, los hidrogeles exhiben aplicaciones potenciales en campos como administración de fármacos [62, 63], remoción de impurezas en soluciones acuosas [64, 65], biosensores [66] y determinación espectrofotométrica de fármacos [67]. Se ha reportado síntesis de hidrogeles a partir de poligliceroles hiperramificados [68, 69] y recientemente, Salehpour sintetizó hidrogeles a partir de poliglicerol [70]; sin embargo, estos hidrogeles se obtuvieron al entrecruzar el poliglicerol con otro polímero, el PEGDE, debido a que el entrecruzamiento del poliglicerol no fue posible con agentes entrecruzantes no poliméricos.

Por otro lado, los absorbentes de solventes no polares, son estructuras tridimensionales entrecruzadas de polímeros hidrofóbicos, que pueden absorber grandes volúmenes de solventes no polares [71]. Se han reportado diferentes estudios de síntesis de oil geles empleando monómeros como cinnamoyl oxietil metacrilato (CEMA), acrilato de octadecilo, dimetacrilato de etilenglicol (EGDMA) y etileno glicol diacrilato (EGDA) y sus aplicaciones están enfocadas hacía la recuperación de petróleo en derrames en corrientes de agua [72-74].

El propósito del presente trabajo de investigación, es estudiar el efecto de las condiciones de reacción en la morfología y propiedades térmicas de los

poligliceroles sintetizados, junto a la cinética de la reacción de polimerización y establecer el efecto de las impurezas del glicerol crudo en el proceso de polimerización. Adicionalmente, se presenta la utilización de ácidos biodegradables tales como el ácido cítrico y el ácido oleico como agentes modificantes de la estructura del poliglicerol sintetizado a partir del glicerol, con el fin de obtener poliglicerol éster que puede ser posteriormente entrecruzado para síntesis de materiales poliméricos absorbentes de solventes polares y no polares. No obstante a que los geles absorbentes han sido previamente estudiados, la novedad de este trabajo en este campo, radica en la utilización de una materia prima abundante y económica, el glicerol, que contribuye a cerrar una cadena productiva renovable.

Este reporte se encuentra dividido en 5 capítulos a través de los cuales se presentan los resultados obtenidos.

En el capítulo 1, *Effect of crude glycerol impurities in the polymerization reaction to produce polyglycerol*, fue evaluado el efecto de las impurezas contenidas en el glicerol crudo, específicamente el contenido de jabones y metales, en el proceso de polimerización a las mismas condiciones de polimerización del glicerol puro, usando ácido sulfúrico como catalizador. Se encontró que el contenido de jabones inhibe la reacción de polimerización del glicerol crudo. Sin embargo, la presencia de metales en el glicerol no causa efectos inhibitorios para la síntesis de poliglicerol.

El capítulo 2, *Study of polyglycerol morphology: dependence on reaction conditions,* se estudió el efecto de las condiciones de reacción, temperatura y concentración del catalizador sobre las propiedades finales del poliglicerol sintetizado: índice de hidroxilo, peso molecular promedio, morfología y temperatura de transición vítrea. Se encontró que la temperatura y la concentración de catalizador tienen un efecto significativo sobre el índice de hidroxilo –indicativo de la funcionalidad del polímero-, sobre la morfología del

poliglicerol y finalmente, sobre la temperatura de transición vítrea del material. Sin embargo, no es significativo el efecto de las condiciones de reacción sobre el peso molecular promedio de los polímeros. Se puede controlar la morfología de los poligliceroles sintetizados, ajustando las condiciones de reacción de polimerización, con el fin de obtener materiales con estructuras determinadas de acuerdo a la aplicación que se requieran.

En el capítulo 3*, Development of a Step-Growth Polymerization Kinetics Model for Polyglycerol Production,* se desarrolló un modelo cinético que describe la polimerización del glicerol para producir poliglicerol. El modelo cinético toma en cuenta dos diferentes resistencias que actúan el paralelo, cada una de las cuales es atribuida a fenómenos diferentes. La primera resistencia es del tipo Arrhenius, con una energía de activación constante, la cual es generada por la reacción química; mientras que se encontró que la segunda resistencia correlaciona el fenómeno físico de la difusión de masa. La reacción de polimerización se monitoreó mediante análisis termogravimétrico. Los cambios en las variables de proceso se discuten en términos del efecto de la velocidad de calentamiento en la entropía del sistema reaccionante.

El capítulo 4, *Synthesis and Characterization of Novel Stimuli-Responsive Hydrogels Based on Polyglycerol*, se enfocó en la síntesis de hidrogeles a partir del entrecruzamiento entre el poliglicerol – derivado del glicerol- y ácidos biodegradables –ácidos cítrico y oleico- con respuesta ante estímulos de pH y temperatura. La respuesta ante estímulos de pH y temperatura está relacionada con la presencia de grupos funcionales específicos y a las temperaturas de transición vítrea, respectivamente. Los hidrogeles sintetizados son amigables con el medio ambiente con una alta capacidad de absorción.

Finalmente, el capítulo 5, *Synthesis and Characterization of Novel Oil-gels Sorbers Based on Polyglycerol,* se enfocó en la síntesis de materiales absorbentes de solventes no polares a partir del entrecruzamiento entre un

derivado del poliglicerol y divinilbenceno. Se estudió el efecto del grado de entrecruzamiento del material y la adición de monómeros como el aceite de palma y el estireno, sobre la capacidad de absorción en tolueno y en soluciones de crudo en tolueno. Los materiales obtenidos son alternativas atractivos debido que son sintetizados principalmente de monómeros biodegradables.

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INTRODUCTION

Development and use of biomass as an alternative energy source to energy produced by petroleum-based fuels has been strongly encouraged by government policies throughout the world [1-3]. Interest has been driven in response to environmental concerns about emissions of greenhouse gases due to the combustion of hydrocarbons [4-6], energy security – threats by continued increases in oil prices- and geopolitical instability in countries with large oil reserves [7].

Biomass is an attractive alternative feedstock for the production of fuels [8, 9], as well as being a potential driving force for development of bio refineries [10-12]. In this context, biodiesel derived from vegetable oils has become an alternative with high potential for the replacement of conventional diesel [13]. Base-catalyzed vegetable oils transesterification process, generally with sodium or potassium hydroxide, involves the triglycerides hydrolysis, in which glycerol molecules are released and become the major co-product of methyl esters production [14].

In the stoichiometry of the vegetable oils transesterification reaction three moles of methanol react with the glycerides in three stages in presence of a catalyst to produce methyl esters and glycerol. In the first stage, methanol reacts with triglycerides to form methyl esters and diglycerides. In the second stage, methanol reacts again, this time with diglycerides to form monoglycerides and methyl esters. Finally in the third stage, monoglycerides react with methanol to form glycerol and methyl esters (Figure 1). According to the reactions described above, one mole of glycerol is produced per 3 moles of methyl esters synthesized. The relation between production of glycerol and formation of methyl esters is approximately 10% by weight [15].

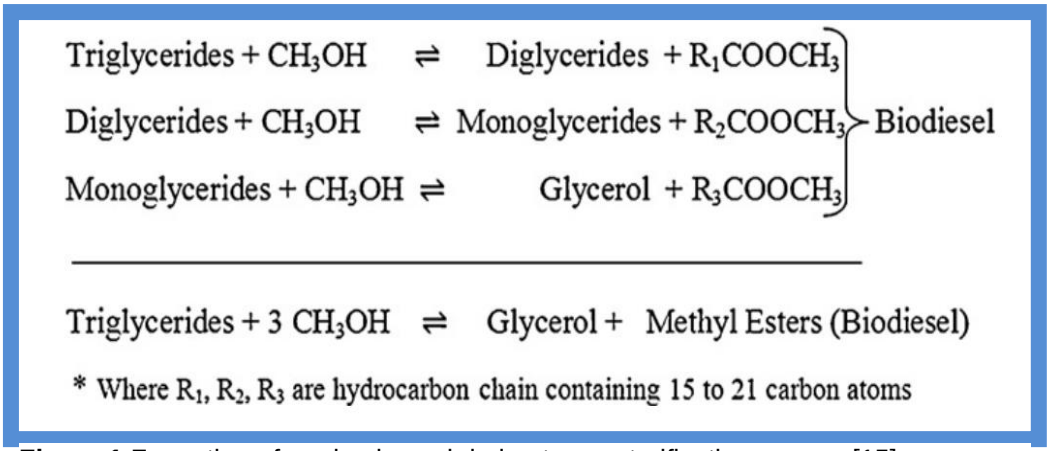

Figure 1 Formation of crude glycerol during transesterification process[15]**.**

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Crude glycerol production is exponentially increasing as a result of growth of biodiesel world production and is projected to reach a 1.54 million tons in 2015 [15]. Oversupply of glycerol has negative effects on the environment [16] and on the profitability of biodiesel production process if not properly managed. Therefore, obtaining products with high value added from glycerol contributes to sustainability and increased profitability for the biodiesel industry, as well as environmental benefits [17, 18].

Currently, glycerol used in industrial applications requires a purity of at least 85%. The purification process to bring the crude glycerol to that purity level represents approximately 14% of total production cost [17]. The high purification costs of crude glycerol to obtain purified glycerol are due to the requirements of separation techniques such as electrochemical [19], ion exchange [20] and vacuum distillation [21] which entail high operation and energy costs. Impurities to remove include catalyst and alcohol residues, free fatty acids, alkyl esters, mono, di and triglycerides [22].

Glycerol application fields, as it is a very versatile compound [23], are mainly in the production of materials with applications in basic chemical industry, industrial microbiology and oxygenated fuel additives such as glycerol carbonate [24, 25];

acrolein [26, 27] and 1,2-propanediol [28, 29]. Additionally, pure glycerol has applications in the food industry, industrial microbiology, pharmacology and cosmetics; however, these applications require purity levels higher that 99%, which implies intensive purification procedures [15]. By contrast, use of crude glycerol as raw material for development of products for industrial use may not require high purification costs. Therefore, researches are currently focused on finding greater value- added uses for crude glycerol that may allow its use in industrial applications such as hydrogen production [30-32], production of polyhydroxyalkanoates (PHAs) [33-36], such as polyol in polyurethane foam production [37, 38], and biogas production [39, 40], in order to transform the current biodiesel industry, into a bio refinery based on the oleochemical industry [41].

Polymerization is a valuable alternative for adding value to glycerol. Polyglycerol is a polymer composed of an inert polyether backbone and an abundance of highly reactive hydroxyl groups which are exposed and allow further modification to produce a variety of related compounds [42-44]. The presence of a catalyst –either of a homogeneous or heterogeneous type that can be either acidic or basic- is required for glycerol polymerization. The direct reaction of analytical glycerol to polyglycerol in the presence of a heterogeneous catalyst, such as solid mesoporous of the MCM- 41 family, has advantages such as easy removal and high selectivity. However, this reaction exhibits low conversion levels, and therefore low molecular weight final products are obtained [45, 46]. With respect to homogeneous catalysts it has been found that when using basic catalysts, carbonates are more active than hydroxides in the polymerization reaction due to better solubility in the reacting mass at high temperatures [47]; acidic-catalyzed homogeneous etherification reactions of glycerol produce polyglycerols with high polymerization. However these are non-selective reactions, and therefore dehydration and oxidation reactions can occur causing end products discoloration [48]. Salehpour and Dubé [49] evaluated the use of sulfuric acid as a catalyst of

glycerol polymerization reactions at reduced pressures and obtained polyglycerols of relatively high molecular weights. Regarding the use of crude glycerol as a polymerization monomer, Ahmad [50] used soap wastes from the transesterification process wastes as reaction catalysts and obtained oligomers of glycerol.

Polyglycerol is industrially produced by ring opening polymerization of glycidol, and polymers with narrow distribution and molecular weights in a range between 1000 and 30000 g/mol are obtained [42, 51-53]. Polyglycerols of higher molecular weight and branched structure directly synthesized from glycerol could replace hyperbranched polymers obtained from glycidol, a toxic monomer [54] opening the possibilities of application at industrial levels for the production of complex hydrophilic, amphiphilic and even hydrophobic polymeric structures. Modifications of hyperbranched polyglycerols, by esterification reactions, have been studied for the preparation of amphiphilic structures. The simple esterification of branched polyglycerols (synthesized from glycerol derivatives) with fatty acids offers potential core-shell amphiphilic structures with applications in biotechnology [55] and removing water-soluble impurities, in non-polar mediums [56]. Furthermore, as polyglycerol esters can have different behaviors ranging from a hydrophilic character to a completely hydrophobic character depending on the degree of esterification of their hydroxyl groups, they are appropriate structures for the design and synthesis of polymeric cross-linked complexes, such as hydrogels and oil-gels. The absorption capacity of these absorbent polymeric materials is due to the presence of free volume within the material structure, which are formed by the crosslinked branched polymer chains which do not allow their dissolution in solvents.

Hydrogels are tridimensional crosslinked hydrophilic polymeric structures that can absorb and retain significant quantities of water [57, 58]. The functional groups present in the structure of hydrogels related with polar solvents are responsible for the swelling and in turn, these functional groups can be used to alter hydrogels

properties in response to environmental stimuli such as Ph, temperature, light, ionic strength, and electric and magnetic fields [59-61]. Because of their water holding capacity and response to environmental stimuli, hydrogels exhibit potential applications in fields such as drug delivery [62, 63], removal of impurities in aqueous solutions [64, 65], biosensors [66] and spectrophotometric identification of drugs [67]. It has been reported synthesis of hydrogels from hyperbranched polyglycerols [68, 69] and recently Salehpour synthesized hydrogels from polyglycerol [70]; however, these hydrogels were obtained by crosslinking the polyglycerol with another polymer, the PEGDE, because polyglycerol crosslink was not possible with non- polymeric crosslinking agents.

Additionally, oil-gels are hydrophobic polymeric crosslinked three-dimensional structures which can absorb large amounts of non-polar solvents [71]. Several studies have reported synthesis of oil gels using monomers such as methacrylate cinnamoyloxyethyl (CEMA), octadecyl acrylate (ODA), ethylene glycol dimethacrylate (EGDMA) and ethylene glycol diacrylate (EGDA); its applications are focused on oil recovery during spills in water streams [72-74].

The purpose of this work is to study the effect of reaction conditions on the morphology and thermal properties of synthesized polyglycerols along with the kinetics of the polymerization reaction, and to establish the effect of impurities of crude glycerol in the polymerization process. Additionally, the use of biodegradable acids such as citric and oleic acids acting as structure modifying agents of polyglycerol, synthesized from glycerol is presented. The purpose was to obtain polyglycerol esters which can be subsequently crosslinked in order to synthesize polymer absorbent materials of polar and nonpolar solvents. Even though absorbent gels have been previously studied, the novelty of this work lies in the use of an abundant and economical raw material, glycerol, which could help close a renewable supply chain.

This report is divided into 5 chapters through which the results of this investigation are shown.

In chapter 1, *Effect of crude glycerol impurities in the polymerization reaction to produce polyglycerol*, was evaluated the effect of impurities of crude glycerol, specifically soap and metal content, on polymerization process at the same conditions of pure glycerol, using sulfuric acid as catalyst. It was found that soap content inhibit polymerization reaction of crude glycerol. However, the metal presence in glycerol does not cause an inhibitory effect on polyglycerol synthesis.

In chapter 2, *Study of polyglycerol morphology: dependence on reaction conditions,* was studied the effect of reaction conditions, temperature and catalyst concentration on final polyglycerol properties: hydroxyl number, average molecular weight, morphology and glass transition temperature. It was found that temperature and catalyst concentration have a significant effect on hydroxyl number –indicative of polymer functionality-, on polyglycerol morphology and finally, on material glass transition temperature. However, the reaction conditions do not have significant effect on average molecular weight. It is possible to control the morphology of synthesized polyglycerols, adjusting reaction conditions of polymerization, with the aim of obtain polymeric materials with determined structures according with their final application.

In chapter 3, *Development of a Step-Growth Polymerization Kinetics Model for Polyglycerol Production,* a kinetic model that describes the polymerization reaction of glycerol to produce polyglycerol was developed. This model takes into account two different resistances acting in parallel; each resistance was attributed to a different phenomena. The first resistance is Arrhenius type, with constant activation energy, which is generated by the chemical reaction; whereas, the second resistance was found to correlate with the mass diffusion physical phenomenon. Polymerization reaction was monitored using thermogravimetry. Changes on the

process variables were discussed in terms of the heating rate effect on the entropy of the reaction system.

The chapter 4, *Synthesis and Characterization of Novel Stimuli-Responsive Hydrogels Based on Polyglycerol,* was focus on the synthesis of hydrogels from the crosslinking between glycerol-derived polyglycerol and biodegradable acids – citric and oleic acids- with response to external stimuli of Ph and temperature. The response to Ph and temperature stimuli is related to specific functional groups presence and glass transition temperatures, respectively. Synthesized hydrogels are environmental friendly with high swelling capability.

Finally, chapter 5, *Synthesis and Characterization of Novel Oil-gels Sorbers Based on Polyglycerol,* was evaluated focus on the synthesis of oil-gel sorber materials from the crosslinking between a polyglycerol-derived material and divinyl benzene. It was studied the effect of crosslinking degree and the addition of monomers as palm oil and styrene on absorption capability in toluene and crude oil in toluene solutions. The obtained materials are attractive alternatives since they are synthesized mainly from biodegradable monomers.

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CHAPTER 1

Effect of crude glycerol impurities in the polymerization reaction to produce polyglycerol

Abstract

Polymerization of crude glycerol, obtained as the major by-product from the biodiesel industry, was studied using the reaction conditions established for polymerization of purified glycerol; however, no polyglycerol was obtained as the reaction product. Consequently, crude glycerol was characterized to identify its composition. An experimental design was performed to study the effect of the most abundant impurities present in crude glycerol on the polymerization reaction, and also the impurities that at the reaction conditions would persist such as soap and sodium. The effect of soap, sodium, and sulfuric acid in the polymerization reaction product using simulated-crude glycerol was studied. The response variable for the experimental design was the hydroxyl number of the reaction products. FT-IR spectroscopy was used to analyze differences among the reaction products obtained from different treatments. The presence of soap was identified to be the main inhibitory factor and the bottleneck in the formation of polyglycerol via polymerization of crude glycerol. Molecular weights of the polymerization reaction products were determined and analyzed with MALDI-TOF technique.

1.1 Introduction

The development of biomass based fuels as an alternative for fossil fuels energy have been worldwide impulse by governmental policies, to diversify the energy sources and to decrease the environmental pollution caused by emissions from combustion of fossil fuels [1, 2]. Therefore, the production of bio-diesel via

transesterification reaction of mainly vegetable oils, has gained considerable attention in recent years. In 2012 the production of bio-diesel was more than 22.4 billion liters and it is expected to increase up to 1.54 million tons by 2015; however, 10% (w/w) of the total production is crude glycerol [3, 4]. If glycerol produced as a byproduct from the transesterification reaction is discarded as waste stream, it could threat the biodiesel production as a cost effective process and would also constitute an environmental threat. Therefore, there is a need to valorize crude glycerol using it in industrial applications. Among some of the already known applications of crude glycerol are: hydrogen production [5-7], synthesis of microbial polyhydroxyalkanoates (PHAs) [8-11], fumaric acid production [12], synthesis of 1,3 – propanediol [13-15], bioconversion into ethanol [16, 17] and polyols for the production of polyurethane [18, 19].

An attractive alternative to use the crude glycerol stream coming from the triglycerides hydrolysis of the biodiesel industry is to transform it into value-added products. A promising valued-added product of glycerol is polyglycerol, a high molecular weight polymer formed by an inert polyether chain with abundant pendant hydroxyl groups that makes polyglycerol a building block for diverse polymeric complexes [20]. One of the main characteristics of polymers made out of polyglycerol is the fact that it is biocompatible, biodegradable, and a sustainable material. However, the reported production of polyglycerol, using sulfuric acid as catalyst, is made from purified glycerol [21]. To the best of our knowledge, synthesis of polyglycerol from crude glycerol as raw material has not been previously reported. The crude glycerol composition shows that 60 to 80% is glycerol and the rest are impurities, mainly classified as soap, water, methanol, catalyst residues, free fatty acids and salts [22]. The purification process of crude glycerol to obtain purified glycerol results in a three times cost increment. The high purification cost is an economic disadvantage that discourages the industrial production of polyglycerol [23, 24].

An attractive alternative to valorize crude glycerol is to produce polyglycerol following the conditions used for polymerization of purified glycerol; however,

according to the present study, production of polyglycerol from crude glycerol as raw material does not occur. This research work seeks to understand and identify the factors that inhibit polymerization of crude glycerol using sulfuric acid as catalyst. For this purpose, a sample of crude glycerol was characterized to identify the impurities. Simulated-crude glycerol was prepared adding the impurities, previously identified into purified glycerol. The effect of each impurity on the polymerization reaction, as well as the interaction between them was analyzed.

An experimental design was performed to study the effect of the most abundant impurities (soap and sodium) and the concentration of catalyst (sulfuric acid) in the polymerization of crude glycerol. It was found that sulfuric acid in presence of soap produce side reactions that compete with polyglycerol synthesis. Furthermore, a statistical analysis to evaluate the effect of the presence and absence of impurities, soap and sodium, at a fixed concentration of catalyst revealed that presence of soap in crude glycerol is the main inhibitory factor of polyglycerol synthesis.

1.2 Materials and Methods

1.2.1 Materials

Pure glycerol and sulfuric acid were obtained from Merck. Crude glycerol, a by-product from biodiesel manufacturing process, was kindly provided by BioSC S.A. biodiesel plant (Santa Marta, Colombia).

1.2.2 Methods

1.2.2.1 Crude glycerol characterization

1.2.2.1.1 Physico-chemical characterization

Density of crude glycerol was determined using a 2 mL pycnometer. The pH of crude glycerol was measured with a digital pH meter Schott HANDYLAB 1 at room temperature (25 $\pm$ 1 ℃).

Glycerol content in the crude glycerol sample was determined using the iodometric–periodic acid method in accordance with AACC 58 technique. Soap content was determined according to a modified version of AOC Cs method [25]. Ash content was determined following the ISO 2098-1972 method.

Water content was determined following the AOCS official method (Ea 8-58), using a Volumetric *Karl Fischer* titrator (Metrohm 870 KF Tritino plus). Presence of methanol was determined by gas chromatography with an Agilent Technologies 6890N system equipped with a flame ionization detector. The method followed was the EN14110. Metals (Ca, K, Mg and Na) were detected by inductively coupled plasma atomic absorption spectroscopy, using a Perkin Elmer 5300 DV spectrometer. These analyses were done in collaboration with the *Quality Inspection Coordination*, ECOPETROL S.A Company.

1.2.2.1.2 Complementary characterization

A thermogravimetric analysis (TGA) was performed to determined polymer degradation as a function of temperature. A temperature range from 25 to 300 ℃ at a heating rate of 5 $℃\,\mathrm{min}^{-1}$ was used. This analysis was performed in a TGA 2050 from TA instruments, Inc., equipped with nitrogen purge gas system $(50\ \mathrm{cm}^3\ \mathrm{min}^{-1})$. Infrared spectrum was obtained in transmittance mode in a Shimadzu 8400s spectrometer. Fatty acid methyl esters present in the crude glycerol sample were identified with a gas chromatography system (Agilent Technologies 6890 series), coupled to a FID detector, using an Agilent DB23 column and SUPELCO 38 FAMES as standards. All measurements were performed in duplicated.

1.3 Experimental procedure

Polymerization reaction was carried out in a 50 mL glass reactor equipped with a nitrogen inlet, catalyst feeding, thermometer inlet, and a distillation trap to continuously remove water from the reaction mixture. Temperature was maintained at 150 ℃ using a temperature-controlled heating bath. A vacuum pump was attached to the reactor through the condenser, while condensation reactions were carried out at pressures below 33.86 kPa during ~ 3 h and before gel point was reached.

1.4 Results and discussion

Three different concentrations of sulfuric acid, 0%, 1%, and 4.8% (% w/w), were used to carry out polymerization reactions of crude glycerol. The viscosity of crude glycerol is 0.28 Pa*s. The highest product viscosity was obtained with the reaction performed with 0% (w/w) sulfuric acid (1.63 Pa*s) compared with the viscosities obtained when using 1% and 4.8% catalyst (0.4 and 1.57 Pa*s respectively). This result can be explained by the presence of soaps in the crude glycerol sample, which catalyzes the oligomerization of glycerol increasing product viscosity [26]. Despite the increase of viscosity in the reaction products, there was not polyglycerol formation under any condition tested. The fact that polymerization of crude glycerol did not happened, even though the reaction was performed under the same conditions for which successful polymerization of purified glycerol was achieved; encourage us to study the factors that inhibit polymerization of crude glycerol. In order to find the polymerization inhibitory factors present in crude glycerol, simulated-crude glycerol samples were prepared according to the composition found in the characterization of crude glycerol.

1.4.1 Characterization of crude glicerol

The physical-chemical characterization of crude glycerol that comes from the hydrolysis of triglycerides in the production of biodiesel indicates that 75% is

glycerol with a pH of 6.14, and a density of 1.28 (g/cm^3). The moisture content determined was 10.5%, soaps content 13.9%, ashes 3.5%, and methanol 0.025%. The presence of metals found in the sample were mainly sodium (22850±3860 mg/Kg), potassium (46.7±3.54 mg/Kg), calcium (17.1±1.78 mg/Kg), and magnesium (8.6±0.68 mg/Kg). Moreover, the free fatty acid (FAMES) composition was formed by palmitic acid 63.3%, oleic acid 29.6%, stearic acid 5.6%, and linoleic acid 1.6%. With regards to metals and FAMES composition, a considerably high amount of sodium with respect to the other metals was observed; likewise, palmitic acid was found in a significantly higher proportion with respect to the other free fatty acids. This increment in sodium and palmitic acid could be explained by the use of sodium hydroxide or methoxide as a catalyst in the transesterification reaction; as well as, the palm oil as a raw material for biodiesel production.

A comparison between Fourier Transform Infra-Red (FT-IR) spectra of crude and purified glycerol is shown in Figure 1.1. The spectra shows the presence of broad OH stretching band from 3000 cm^{-1} to 3600 cm^{-1}, C-H stretching between 2883 to 2947 cm^{-1} and C-O stretching from 1040 to 1120 cm^{-1} (Figure 1.1A). A carboxyl (COO-) peak only appears in the crude glycerol sample, see Figure 1.1B. This peak might be due to the pH reduction during the acidification stage of crude glycerol, where most of the soaps were converted to insoluble and uncharged free fatty acids [27, 28]. The thermogravimetric analysis reveals a 2.45% weight loss in a temperature range between 25-37°C. This weight loss is due to the presence of volatile materials such as methanol. From 37-94°C, there is a 9.46% weight loss due to water evaporation, and between 100-200 °C, there is a significant weight loss attributed to glycerol thermal degradation. The remnant mass observed in the thermogram after 200 °C might be explained by the presence of inorganic salts and fatty acids, as reported in previous studies [29, 30].

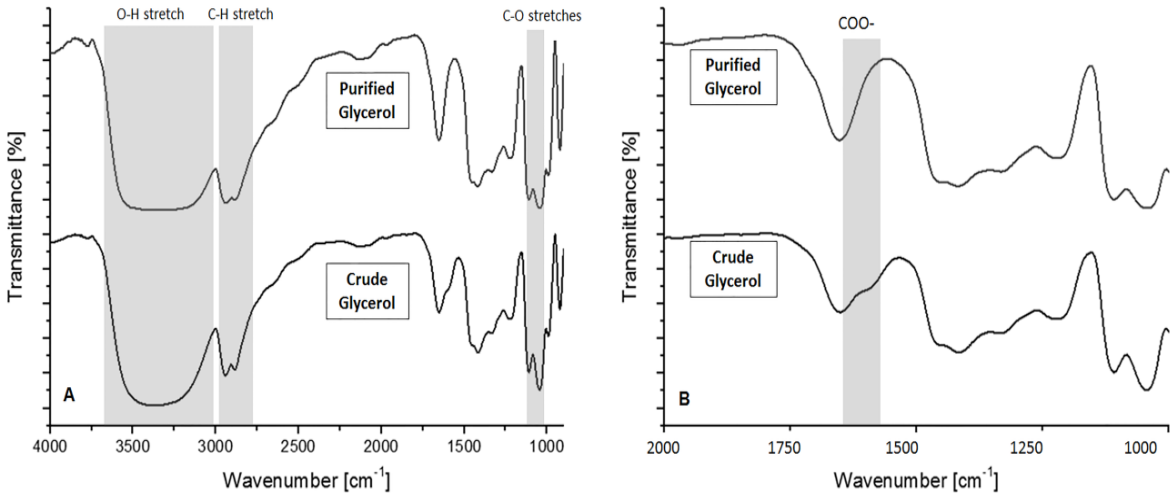


Figure 1.1 FT-IR spectra of crude and purified glycerol. Figure 1.1A shows the presence of stretching bonds in the samples analyzed. Figure 1.1B shows a carboxyl (COO-) peak that appears only in the crude glycerol sample.

1.4.2 Simulation of crude glycerol composition

Based on the composition obtained from the characterization of crude glycerol, a simulated-crude glycerol sample was prepared by adding the impurities into purified glycerol. Soaps and metals were the most abundant impurities identified and considering that at 150°C, water and methanol have been evaporated, the last two were not considered to affect the polymerization of crude glycerol to produce polyglycerol. The soap used to simulate crude glycerol was made from palm oil saponification [31], and the metal was sodium because in the characterization of crude glycerol, it was in a considerable higher amount in comparison with other metals. The simulated-crude glycerol was prepared by adding soap at 14%w/w, and sodium at 22850 mg/Kg.

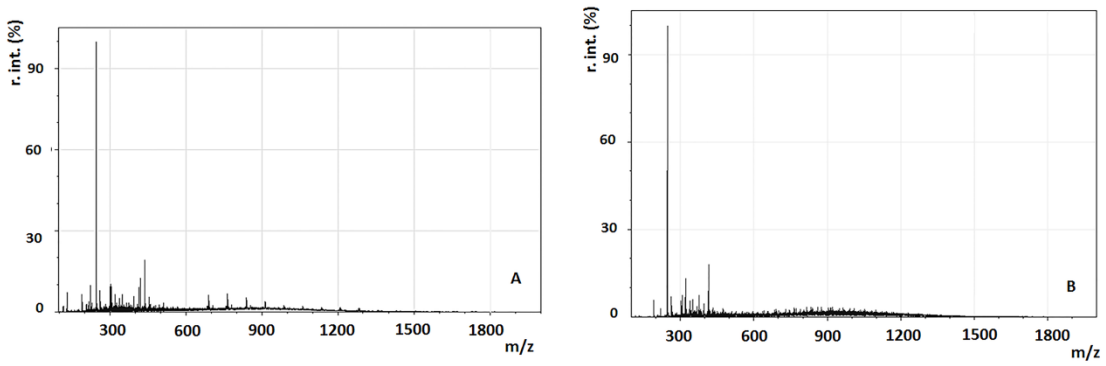


Figure 1.2 Electrospray Ionization (ESI) mass spectrum comparison between the polymerization reaction products of characterized (A) and simulated (B) crude glycerol. The concentration of sulfuric acid used as catalyst was 4.8% w/w.

To confirm if the simulated crude glycerol prepared resembles the crude one, two polymerization reactions were conducted under the same conditions using as raw materials the simulated and characterized crude glycerols. The catalyst used was sulfuric acid at 4.8% w/w. Polymerization reactions were performed under the conditions already established in preliminary experiments to produce polyglycerol from purified glycerol. Hydroxyl number, mass spectroscopy, and thermogravimetry analysis were performed to compare reaction products obtained from polymerization reaction of the simulated and characterized crude glycerols. Results show a similar hydroxyl number for both glycerols used, simulated and the characterized one, which correspond to 376.25 ± 6.68 and 406.76 ± 7.35 mg KOH/g respectively. Mass spectroscopy peaks for both samples were comparable (Figure 1.2A-B). TGA analysis showed similar weight loss profile as a function of temperature, see Figure 1.3 A and B.

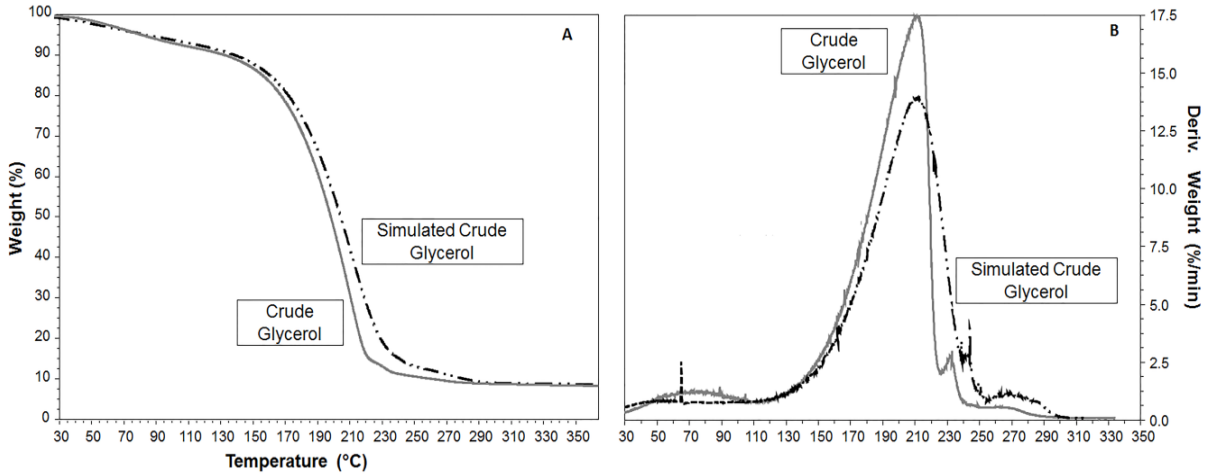


Figure 1.3 TGA (1.3A) and the first derivative of TGA curves (1.3B) of the reaction products from polymerization reaction of characterized and simulated-crude glycerol. Similar weight loss profile of the two samples was observed.

1.4.3 Effect of sulfuric acid, sodium, and/or soap in the polymerization reaction of simulated-crude glycerol

A 2^k full factorial experimental design was performed to determine the effect of the presence and absence of catalyst and impurities in the polymerization reaction of simulated-crude glycerol as raw material. Table 1.1 summarizes the factors and levels used in the experimental design. Samples for each treatment were prepared adding the impurities corresponding to the factor levels proposed in the factorial design into purified glycerol. The reaction procedure was carried out as described in the experimental procedure section.

Table 1.1 2^k experimental design layout.

Factors	Levels	
	Low	**High**
(A) Soap [%w/w]	10	14
(B) Sodium [mg/Kg]	0	22850
(C) Sulfuric acid [%w/w]	0	4.8

The hydroxyl number of the reaction products was selected as response variable, since it is an indicator of etherification or esterification reactions that may occur from different treatments. If in a treatment, an etherification or esterification reaction occurred, the hydroxyl number of the product should decrease with respect to the initial hydroxyl number of glycerol, because some of the initial OH groups have reacted. The chosen response variable may also suggest the formation of polyglycerol, since this polymerization reaction is an etherification. The hydroxyl number of the reaction products for each treatment was determined following the ASTM D 4274-11 method. The hydroxyl number of purified glycerol is 1800 [mg KOH/g] [32]. Data reported in Table 1.2 is the average of two replicates which deviate less than 5% in all the treatments.

Table 1.2 Treatments, levels, and response variable of the 2^3 factorial design. Two independent samples were performed per treatment.

Treatments	**FACTORS**			**Hydroxyl number value [mg KOH/g]**
	Soap (A) % w/w	**Sodium (B) mg/kg**	**Sulfuric acid (C) % w/w**	
(1)	10	0	0	1780.97 ± 7.01
a	14	0	0	1446.40 ± 13.01
b	10	22850	0	1728.19 ± 12.12
ab	14	22850	0	1725.86 ± 52.34
c	10	0	4.8	339.15 ± 3.15
ac	14	0	4.8	318.21 ± 4.03
bc	10	22850	4.8	725.03 ± 0.28
abc	14	22850	4.8	376.25 ± 6.68

The analysis of variance for the factorial design is presented in Table 1.3. Results from statistical analysis suggest that factors affecting the hydroxyl number are, in order of importance, sulfuric acid, soap, and sodium. The interactions between sodium and sulfuric acid, and between the three factors (soap, sodium, and sulfuric acid) are also significant. The effect caused by the interaction between

the other factors not mentioned above in the hydroxyl number is negligible. Results suggest that the presence of sulfuric acid propitiates reactions that end up in products with a smaller hydroxyl number than glycerol. As the soap content in the simulated crude glycerol increases from 10% to 14 % (w/w), the hydroxyl number of the reaction products decreases. On the other hand, the presence of sodium at 22850 mg/kg and the interaction between sodium and sulfuric acid when it goes from no sodium, neither sulfuric acid to 22850 mg/kg of sodium and 4.8 % (w/w) sulfuric acid causes the hydroxyl number of the reaction product to increase. Finally, the interaction between soap, sodium and sulfuric acid when they go from 10% w/w soap in the absence of sodium and sulfuric acid to a 14% (w/w) soap, 22850 mg/kg sodium, and 4.8% sulfuric acid, the hydroxyl number of the products decrease.

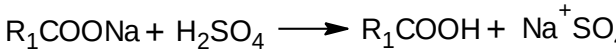
Table 1.3 Statistical analysis of the factors effect on the hydroxyl number of the reaction products and analysis of variance.

Factors	Effect on hydroxyl number	P – value
A	-88.33	< 0.0001*
B	83.83	< 0.0001*
C	-615.35	< 0.0001*
AB	0.55	0.9574
AC	-4.10	0.6913
BC	27.15	0.0260*
ABC	-82.51	< 0.0001*

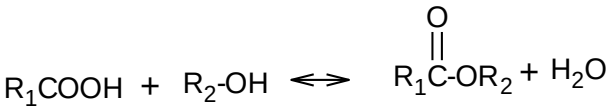
***The factor have significant effect on the response variable ($p<0.05$)

The reaction products obtained from the treatments proposed in the experimental design were analyzed with FT-IR. The spectrum obtained confirmed that the decrease in the hydroxyl number in the treatments was not due to polyglycerol formation but to other chemical reactions. The FT-IR spectra performed to all reaction products are presented in Figure 1.4. The spectra

obtained from the reaction products formed are different from the polyglycerol spectra reported in this study, as well as in others [21]. In the spectrum of treatment (ac), where sulfuric acid and soap factors were 4.8 % w/w and 14 % w/w respectively, there is a pronounced peak in 1735 cm^{-1}. We hypothesize that in these cases sulfuric acid does not act as a catalyst and becomes a reactant that with soap forms free fatty acids. These free fatty acids react with glycerol forming esters, as shown in equations 1 and 2. These chemical reactions under similar conditions have been reported to occur in previous studies [33, 34]. For treatments (a), (b) and (ab), where sulfuric acid was absent (0% w/w) in the mixture, there is a C-O-C ether stretching peak in the range between 1290 to 1100 cm^{-1}. This result may indicate glycerol oligomerization catalyzed by soaps, as previously reported [26].



(1)



(2)

Table 1.4 Treatments, levels, and response variables of the 2^2 factorial design. Sulfuric acid was fixed at 4.8% w/w. The data reported is the average of two replicates which deviated less than 1% for all the treatments.

Treatments	Factors		Hydroxyl number value [mg KOH/g]
	Soap %w/w A	Sodium mg/kg B	
(1)	0	0	448.58± 11.64
a	14	0	318.21± 4.03
b	0	22850	424.36± 0.01
ab	14	22850	376.25± 6.68

In the former experimental design, all the treatments contained soap. To study the effect of the presence and absence of soap in the simulated crude glycerol sample, another experimental design was performed, where soap and sodium were the factors. The concentrations of sulfuric acid was fixed at 4.8% (w/w), since at this concentration of sulfuric acid, polyglycerol was successfully synthetized in previous works using purified glycerol [21]. Table 1.4 shows the concentrations of the factors analyzed (levels) and the response variable of the factorial design, which was again the hydroxyl number of the reaction product. The data reported is the average of two replicates which deviated less than 1%.

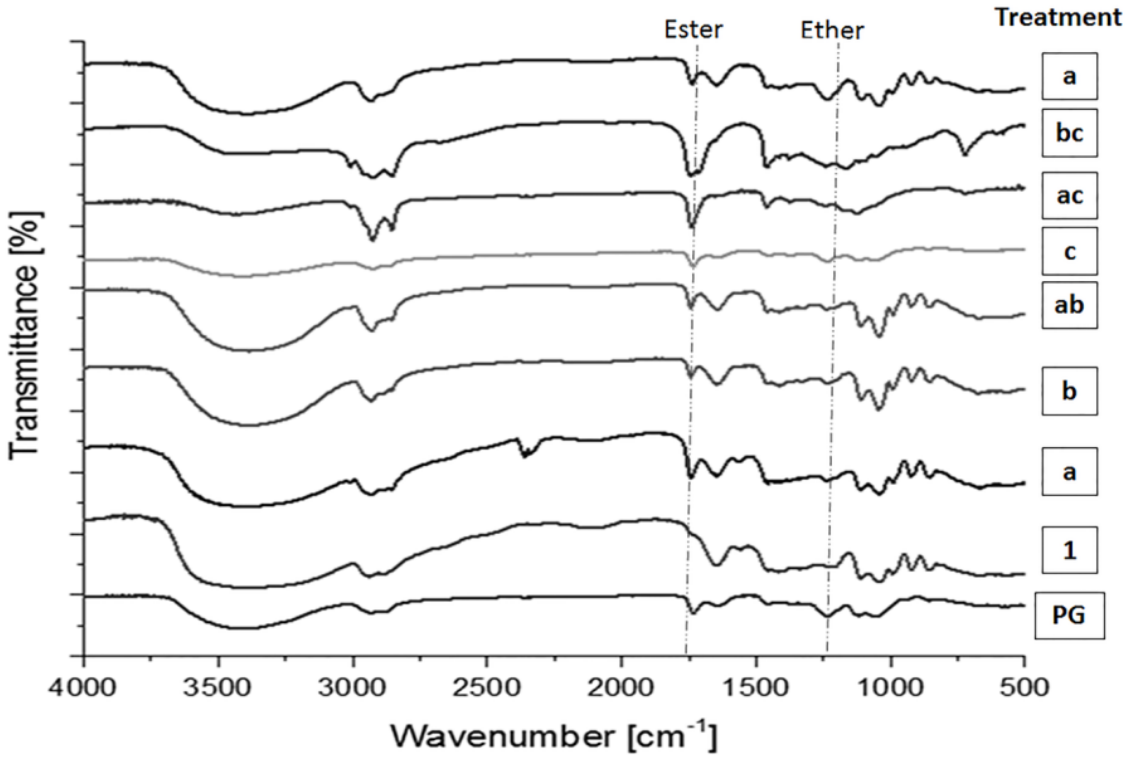


Figure 1.4 FT-IR spectra of the eight treatments proposed in the 2^3 factorial design.

The analysis of variance reveals that presence of soap as well the interaction between sodium and soap, affect the hydroxyl number, see Table 1.5. The increment of soap from 0% to 14% (w/w), decreases the hydroxyl number of the reaction product from 448.58±11.64 to 318.21±4.03. In absence of soap, the effect of sodium in the hydroxyl number is negligible; whereas, when sodium and

soap are present, the interaction between these factors causes a significant effect increasing the hydroxyl number. The FT-IR spectra of the products obtained from the reactions in the absence of soap (treatment (1) and (b) presented in table 4), are similar to the reported polyglycerol spectra [21], see Figure 1.5. On the other hand, as expected from the former experimental design, the FT-IR spectrum of treatments where soap was present showed an ester peak that is consistent with the explanation given from previous results.

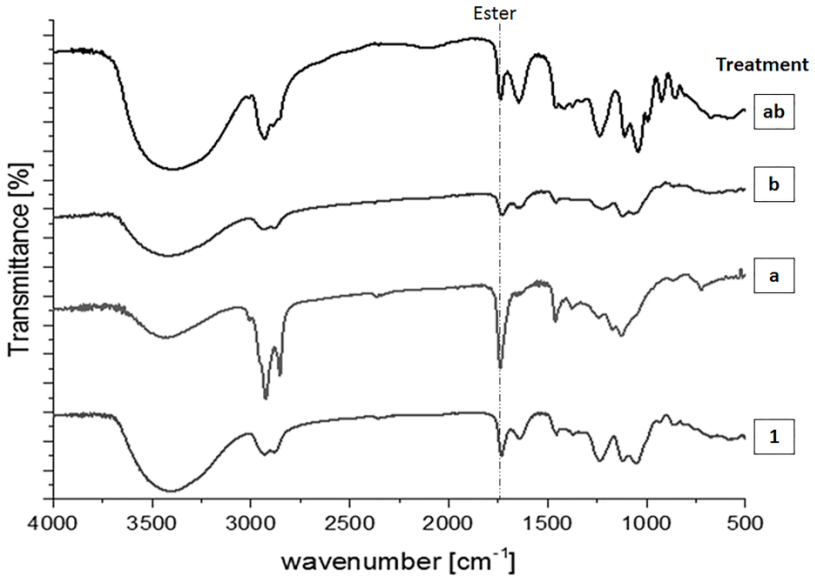


Figure 1.5 FT-IR spectrum of the four treatments proposed in the 2^2 factorial design. FT-IR spectrum of the product obtained from the reaction in the absence of soap (treatment b) is similar to the reported polyglycerol spectrum [21].

Table 1.5 Statistical analysis of the factors effect on the hydroxyl number of the reaction product.

Factors	Factor effect	P – value
A	-44.62	0.0008*
B	8.45	0.1630
AB	20.56	0.0142*

***** The factor have significant effect on the response variable ($p<0.05$)

From these results, it can be conclude that in the absence of soap, the reduction in the hydroxyl number of the reaction product is due to a polymerization reaction that forms polyglycerol. Figure 1.6 shows the molecular weight distribution of treatments were soap was absent in the reaction (treatment (1) and (b)) using a MALDI- TOF analysis. Polyglycerol molecular weight distribution in absence of soap and in presence of sodium (treatment (b)) ranges between 2800 to 4100 Da. Polyglycerol molecular weight distribution in absence of soap and sodium (treatment (1)) ranges between 2700 to 4400 Da. These results are consistent with the number average molecular weight of polyglycerol previously reported [21]. Results from this study suggests that removing the soap from crude glycerol and using sulfuric acid as catalyst under the reaction conditions described in the experimental procedure section, it is possible to synthesize polyglycerol. Therefore, the bottleneck for successful polymerization of crude glycerol to produce polyglycerol is soap removal.

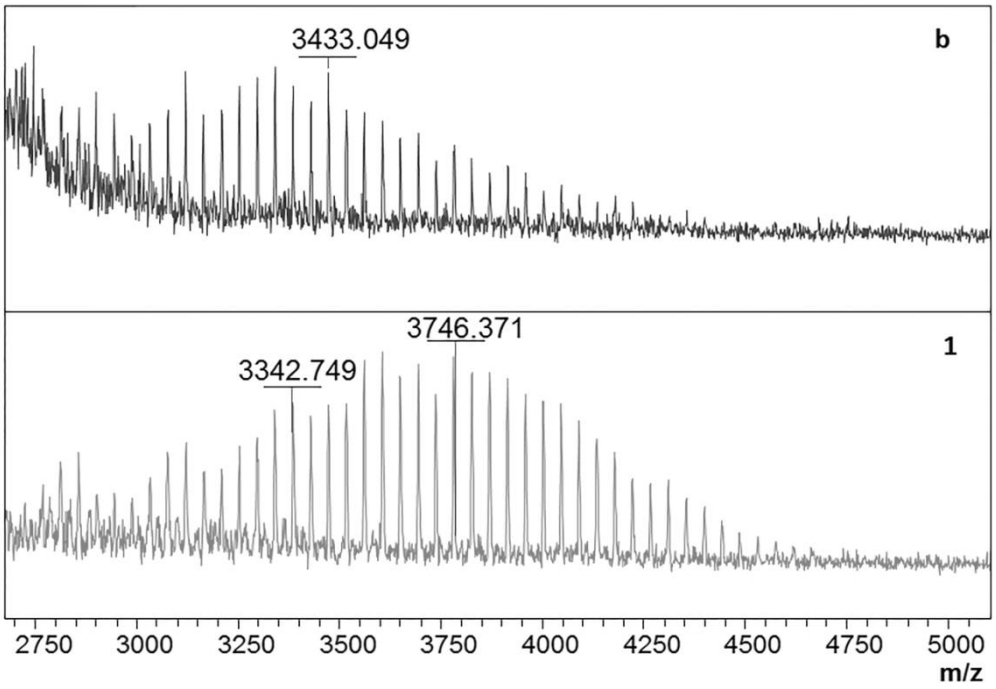


Figure 1.6 MALDI- TOF analyses of the products obtained from treatments were soap was absent in the reactions (treatment (1) and (b) established in the 2^2 factorial design).

1.5 Conclusions

Soap and sodium are the most abundant impurities present in crude glycerol and also the impurities that affect the most polyglycerol synthesis because of the reaction conditions. A statistical analysis confirmed a significant effect cause by three factors: soap, sulfuric acid, and sodium, as well as the interactions between the first two and all the three factors on the hydroxyl number of the reaction product. FT-IR analysis showed that when crude glycerol contains soap, changes in the hydroxyl number of the products formed were not due to polyglycerol. This happens because of other side reactions between soaps and sulfuric acid (catalyst), which compete with the reaction where polyglycerol is synthesized. The effect of soap and sodium in the product formed, revealed that soap is the main factor inhibiting polyglycerol synthesis. MALDI-TOF analysis confirmed that polymerization of crude glycerol in the absence of soap results in polyglycerol synthesis.

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CHAPTER 2

Study of polyglycerol morphology: dependence on reaction conditions

Abstract

The effect of the reaction conditions on glycerol-derived polyglycerol morphology was studied using the temperature and the catalyst concentration as factorial design experiment factors. The response variable for the experimental design was the hydroxyl number of the reaction products. FT-IR spectroscopy was used to analyze main functional groups of polyglycerol. Molecular weights of the obtained polyglycerol were determined and analyzed with MALDI-TOF technique. Quantitative ^{13}C NMR analysis was employed to study the differences on morphology of synthetized polyglycerols. Glass transition temperatures behaviors of polyglycerols were determined with DSC analysis. Temperature and catalyst concentration as well as their interaction affect final hydroxyl number, morphology and glass transition temperature of synthesized polyglycerols. However, no effects were observed on molecular weights distribution of products.

2.1 Introduction

Polyglycerol is a promising bio-based polymer used as a building block for many applications, such as hydrogels [1-3], emulsifiers [4, 5], catalyst supports [6] and biomedical applications [7-9]. The interest for polyglycerol synthesis is based on its high number of functional groups and versatility for future polymeric complexes production. The polyglycerol herein studied, is produced via step-growth polymerization of glycerol using sulfuric acid as catalyst. Properties of polyglycerol-based materials are highly influenced by the polyglycerol morphology. Control of glycerol polymerization to selectively produce a desire polyglycerol

material with a specific morphology is a scientific challenge which may depends on the synthesis conditions. The purpose of this work is to study and understand the effect of synthesis conditions on the polyglycerol morphology.

Using glycerol as starting raw material for polyglycerol synthesis, a value-added polymer, is a significant contribution to the development of environmental safe polymeric materials, since glycerol is nontoxic, biosustainable, and a biodegradable compound [10]. Polyglycerol can also be obtained via one-step anionic ring-opening polymerization of glycidol, resulting in hyperbranched polymers with high molecular weight and narrow polydispersity [11, 12]; however, they are less attractive than the polymeric materials produced via etherification of glycerol due to environmental concerns. It has been reported that sulfuric acid homogenous catalyst yields relatively high molecular-weight polyglycerols [13]; therefore, sulfuric acid was selected to catalyze the reaction that gives formation to polyglycerol. Previous studies on the morphology of glycerol etherification derivatives have been conducted with a comprehensive ^{13}C NMR spectroscopy study of glycerol oligomers morphology, where carbons assignments for linear, branched, and cyclic structures have been found [14]. Likewise, similar carbon assignments for linear, branched, and cyclic structures were found in synthesized polyglycerol chains using ^{13}C NMR spectra [13]. In this study, the appearance of peaks related to branched structures suggests that the homogeneous acid-catalyzed polymerization of glycerol at high temperatures favors the occurrence of branched structures.

The present study seeks to understand and elucidate how temperature and concentration of catalyst affect the morphology of produced polyglycerol. An experimental design was performed to analyze variations in process variables such as, hydroxyl number, molecular weight distribution, degree of branching, and thermal behavior of produced polyglycerol as a function of synthesis conditions. MALDI-TOF spectrometry, NMR spectroscopy and differential scanning calorimetry analysis were the tools used to perform the analyses. As a result, the relation

between polyglycerol morphology and synthesis conditions is established. Additionally, it is concluded that hydroxyl number, branching and glass transition temperature, essential parameter influencing material properties, may be tuned for specific applications during the synthesis conditions.

2.2 Materials and Methods

2.2.1 Materials

Glycerol (85%) and Sulfuric acid (95%) were obtained from Merck. Purified glycerol was roto-evaporated to remove water. Acetic Anhydride was obtained from Carlo Erba, Pyridine (99.5%) from Mallinckrodt, Phenolphthalein Indicator from Merck and Sodium Hydroxide (99%) from Merck.

2.2.2 Experimental procedure

Polymerizations were carried out in a 50 mL glass reactor equipped with a distillation trap to continuously remove water from the reaction mixture, nitrogen, catalyst feeding and thermometer inlets. Glycerol polymerization reaction temperature was varied in a range from 130 to 170 ℃ using a temperature-controlled heating bath. A vacuum pump was attached to the reactor though the condenser to perform the reactions at pressures below 22 kPa.

2.2.3 Characterization

Hydroxyl number was calculated according to ASTM D 4274-11 method. Polymer sample was acetylated with an acetic anhydride-pyridine solution. The unreacted acetylation reagent was hydrolyzed with water and the acetic acid titrated with standard sodium hydroxide solution. The hydroxyl content was calculated from the difference in titration between blank and sample solutions.

Matrix-assisted laser desorption and ionization time-of-flight (MALDI-TOF-MS) measurements were performed with a Bruker Reflex mass spectrometer, equipped with a nitrogen laser delivering 3 ns laser pulses at 337 nm. Recrystallized α-Cyano-4-hydroxycinnamic acid (10 mg/mL) in 30:70 (v/v) acetonitrile/water

containing 0.1% (v/v) TFA, was used as the matrix. Sodium chloride solution was used as cationization agent. Polymer samples were dissolved in water (10 μg/mL). An aliquot of the matrix (0,8 μL was applied to a multistage target until solvent evaporation. Subsequently, 0,1 μL of cationization agent and 0,2 μL of sample were added. The ^{13}C NMR quantitative spectra were taken on a Bruker Untrashield 400 MHz (Avance III, 400). DEPT technique (Distortionless Enhancement by Polarization Transfer) was used to determine peaks multiplicity. Samples were prepared by dissolving the polymer in deuterated water at a concentration of 250 g/L.

Differential Scanning Calorimetry measurements were carried out on a Differential scanning calorimeter Discovery, TA Instruments, Inc. (USA), modulated DSC experiment. Modulated amplitude temperature was 1 °C, a period of 60 seconds in a temperature range from -10°C to 300 °C at a heating rate of 3°C/min and nitrogen purge gas (50 mL/min). Fourier transform infrared Spectroscopy (FTIR) was used to identify functional groups present in the reaction products. The infrared spectra were obtained in transmittance mode in a Thermo Scientific spectrometer (Nicolet 1550 FT-IR).

2.3 Analysis and results

2.3.1 Catalyst concentration and temperature effect on polyglycerol hydroxyl number

A 3^k full factorial experimental design was performed to determine the effect of temperature and catalyst concentration in the hydroxyl number of resulting polyglycerol. The hydroxyl number selected as response variable indicates the number of hydroxyl functional groups present in synthetized polyglycerol defining the polymer hydrophilic component and hydrophilic-hydrophobic balance (HLB) of future products based on this polyglycerol. Temperature and catalyst concentration were evaluated at three levels: (i) temperature: 130°C, 150°C and 170°C and (ii) catalyst: 1.5 w/w%, 3.35 w/w% and 5.2 w/w%, see table 2.1. Samples were

randomized and three replicates per level were performed. The reaction procedure was carried out as described in the experimental procedure section.

Table 2.1 3^k experimental design layout

Parameter	Levels		
Temperature [°C]	130	150	170
Catalyst [w/w%]	1.5	3.35	5.2

Despite the non-selectivity of sulfuric acid as catalyst that may leads to side reactions such as oxidation and dehydration [15, 16], polyglycerol was the main product obtained under the synthesis conditions described in the experimental procedure section. The homogeneous acid–catalyzed step-growth polymerization of glycerol proceeds by splitting a water molecule for each ether link formed. As a consequence, the hydroxyl number of the glycerol polymerization product should decrease with respect to the initial hydroxyl number of glycerol [17]. Results of hydroxyl number of produced polyglycerol at different temperatures and catalyst concentrations are shown in Table 2.2. Furthermore, Figure 2.1 shows the effect of synthesis conditions, i.e., temperature and catalyst concentration, on the response variable, the hydroxyl number of produced polyglycerol.

Table 2.2 Factors levels and response variable of 32 factorial design. The factors are temperature (°C), and sulfuric acid (w/w %). The hydroxyl number of pure glycerol is 1800 [mg KOH/g] [18]. A series of nine experiments were carried out in triplicate.

Temperature °C	Catalyst w/w %	Hydroxyl number value mg KOH/g
130	1.5	610 ± 20
130	3.35	441 ± 4
130	5.2	566 ± 12
150	1.5	525 ± 28
150	3.35	506 ± 22
150	5.2	390 ± 13
170	1.5	413 ± 23
170	3.35	318 ± 29
170	5.2	370 ± 20

The full factorial statistical analysis showed that temperature (P- value < 0.0001), catalyst concentration (P- value: 0.0007) and the interaction between the two factors (P- value: 0.0031) had a significant effect on the produced polyglycerol hydroxyl number. Temperature is the factor with the greatest effect on the hydroxyl number of produced polyglycerol. For instance, at fixed catalyst concentration of 5.2 w/w% and temperatures of 130°C, 150°C, and 170°C the calculated hydroxyl numbers of produced polyglycerol were 566.070 $\pm$ 12.37, 390.123 $\pm$ 13.33, and 370.606 $\pm$ 20,73 mg KOH/g, respectively. This result suggests that an increment of the reaction temperature causes a reduction in the hydroxyl number of polyglycerol. Furthermore, at fixed temperature of 150°C and catalyst concentration of 1.5, 3.35 and 5.2 w/w% the calculated hydroxyl number of produced polyglycerol were 525.777 $\pm$ 28.35 mg KOH/g, 506.029 $\pm$ 22.96 and 390.123 $\pm$ 13.33 mg KOH/g, respectively. The effect of catalyst concentration on the hydroxyl number of produced polyglycerol could be related to the number of protons (H^+) available to perform a nucleophilic attack on glycerol molecules. These results suggest that temperature, catalyst concentration, and their interaction affect the number of pendant hydroxyl groups –the number of functional groups- of produced polyglycerol.

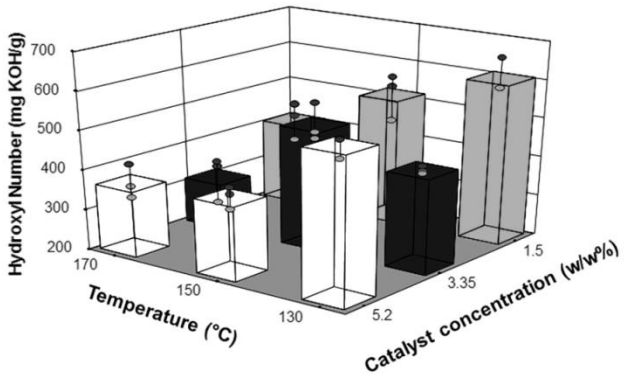


Figure 2.1 Effect temperature and catalyst concentration on the hydroxyl number of the product obtained from glycerol polymerization reaction at three different temperatures and catalyst concentrations.

2.3.2 Infrared spectroscopic analysis FT-IR

Fourier transform infrared Spectroscopy (FT-IR) analysis confirms that the functional groups of the studied reaction products of glycerol polymerization catalyzed by sulfuric acid are similar to the ones present in polyglycerol. The FT-IR spectra of two representative samples are shown in Figure 2.2. The samples correspond to the products of glycerol polymerization performed at 130, 170 °C and catalyst concentrations of 1.5 and 5.2 w/w %, respectively. The obtained spectra are similar to reported polyglycerol spectra [1], where absorptions at 3000 cm^{-1} to 3600 cm^{-1} (OH stretching band) are related with polyglycerol terminal hydroxyl groups, broad alkyl stretching bands (C-H) are observed at 2883 and 2947 cm^{-1}, and absorptions ranged from 950 to 1150 cm^{-1} (C-O stretching) are related to polyglycerol ether backbone.

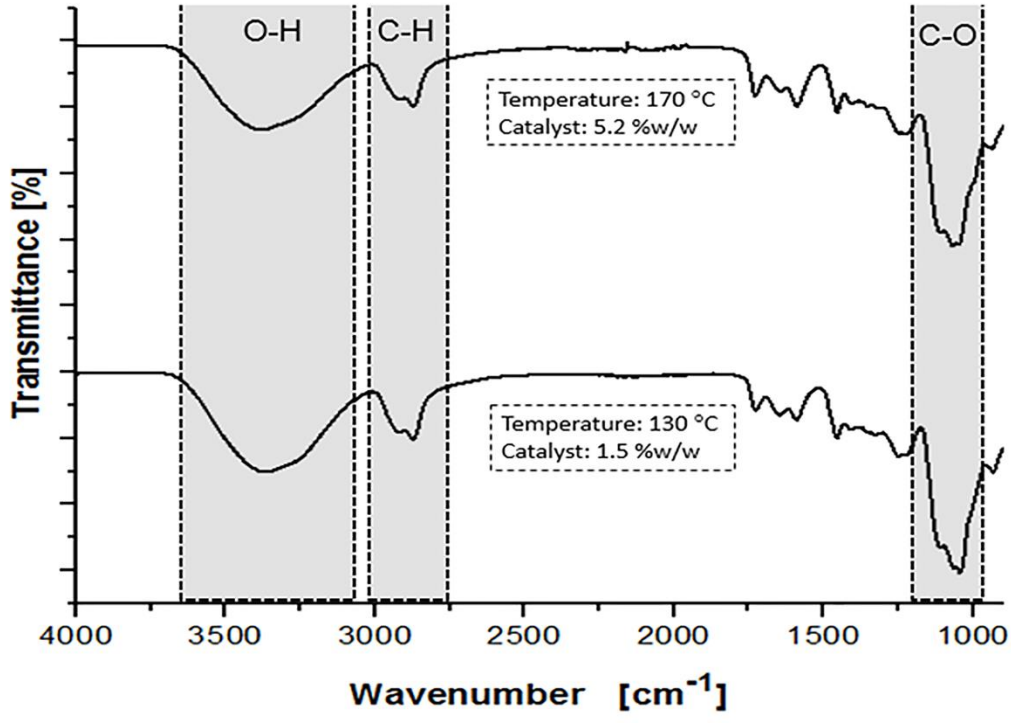


Figure 2.2 FT-IR spectra of two representative products of glycerol polymerization performed at different synthesis conditions. First reaction was carried out at 130 °C, and catalyst concentration of 1.5 w/w % . Second reaction was carried out at 170 °C and catalyst concentration of 5.2 w/w %. The obtained spectra are similar to reported polyglycerol spectra **[1]**.

2.3.3 Molecular Weight Distribution of synthetized polyglycerol

The effect of synthesis conditions, temperature and catalyst concentration on polyglycerol molecular weight distribution and polydispersity were studied. The number and weight average molecular weights, as well as the polydispersity of each treatment established by the factorial design are shown in Table 2.3. From the results, it is observed that the temperature and catalyst concentration in the evaluated range have not a significant effect on polyglycerol average molecular weight and polydispersity. Figure 2.3 shows the MALDI-TOF mass spectra analysis of treatments with temperature of 130, 170 °C and catalyst concentration of 1.5 and 5.2 w/w % respectively. This two treatments exhibit similar molecular weight distributions and polydispersities. The molecular weights determined for all the treatments are according with reported number average molecular weights of polyglycerol at 140°C and pressures below 26kPa [13].

Table 2.3 Polydispersity, number and weight average molecular weights of polyglycerol synthesized at three different temperatures (130, 150, and 170°C) and catalyst concentrations (1.5, 3.35, and 5.2 w/w %).

Temperature °C	Catalyst w/w%	Mw [Da]	Mn [Da]	PD
130	1.5	2987.155	2919.151	1.023
130	3.35	2986.523	2917.573	1.024
130	5.2	2976.242	2908.934	1.023
150	1.5	2978.194	2910.320	1.023
150	3.35	2978.312	2911.348	1.023
150	5.2	3012.363	2943.237	1.023
170	1.5	2991.133	2924.485	1.023
170	3.35	2975.657	2908.184	1.023
170	5.2	2982.514	2917.250	1.022

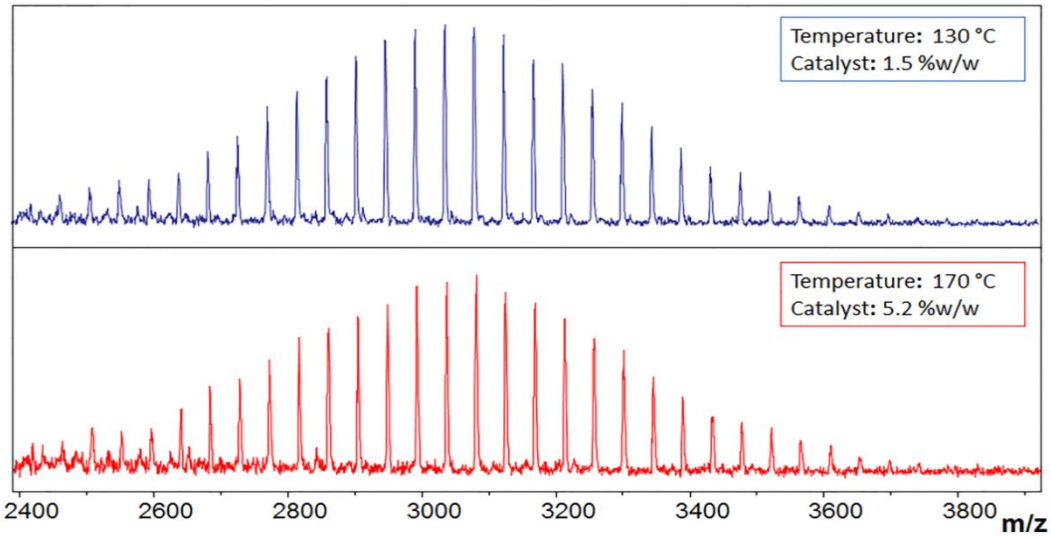
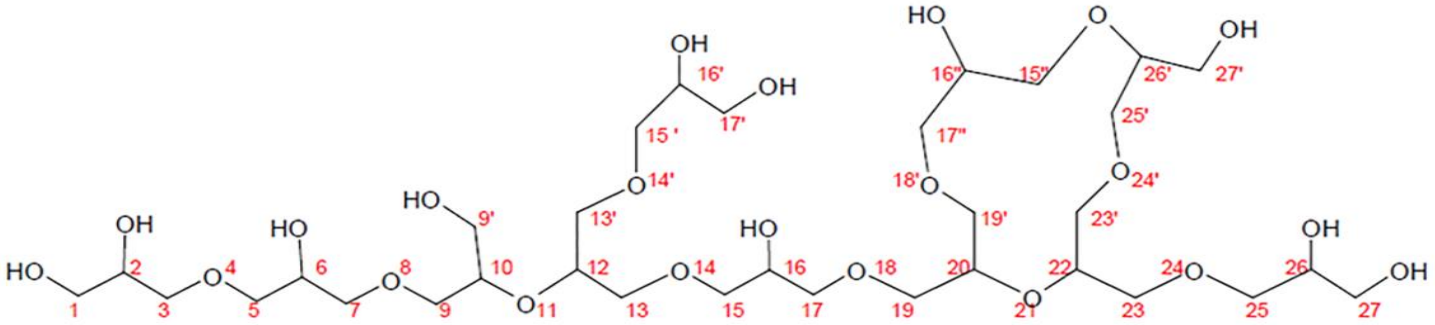


Figure 2.3 Molecular weight distributions determined with MALDI-TOF spectra of two polyglycerol samples: treatments with temperature of 130, 170 °C and catalyst concentration of 1.5 and 5.2 w/w % respectively.

2.3.4 Polyglycerol branching analysis

Polyglycerol samples obtained under the different conditions herein tested were analyzed with ^{13}C nuclear magnetic resonance (NMR) spectroscopy to identify presence of branched structures. Peak analysis between quantitative ^{13}C NMR and DEPT spectra was made to establish whether ^{13}C NMR carbons were methylene (CH_2) or methine (CH) [19]. As reported in other studies [11, 14], the ^{13}C- NMR spectra signals were assigned in different regions of polyglycerol structure as follows: -CH_2OH carbons of terminal chains in 60 to 64 ppm, -CHOH- carbons in 68 to 73 ppm, -CH_2-O- carbons at 72 to 73 ppm and –CH-O carbons - which are related with the beginning of branched chains- at 74 to 82 ppm region, see Table 2.4. Quantitative ^{13}C NMR and DEPT spectra of treatment performed at 130 °C and catalyst concentration of 1.5 w/w% are shown in Figures 2.4 and 2.5, respectively. Figure 2.4 shows a single peak at 81 ppm (-CH-O region) which confirms the presence of branched structures in resulting polyglycerol.

Table 2.4 Model of glycerol polymerization growing chain containing linear, branched and cyclic segments and their carbons assignments in ^{13}C NMR [11, 13, 14].

Carbon type (δ ^{13}C in ppm)			
			
-CH_2OH	**-CHOH-**	**-CH_2-O-**	**-CH-O-**
60-64 ppm	**68-73 ppm**	**72-73 ppm**	**74-82 ppm**
C-1, C-9, C-17', C-27, C27'	C-2, C-6, C-16', C-16'', C-26	C-3, C-5, C-7, C-9, C-13, C-15, C-13', C-15', C-17, C-19, C-19',C-17'', C-23, C-25, C-15'', C-26', C-25', C-23'	C-10, C-12, C-20, C-22

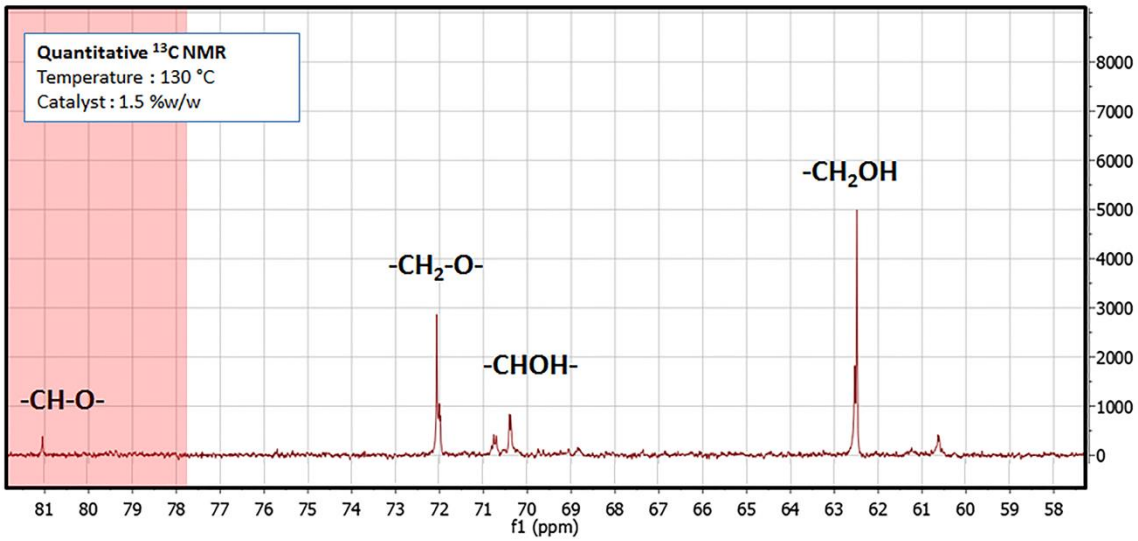


Figure 2.4 Quantitative ^{13}C NMR spectra of the polyglycerol synthetized at 130 °C and catalyst concentration of 1.5 w/w% (Treatment 5).

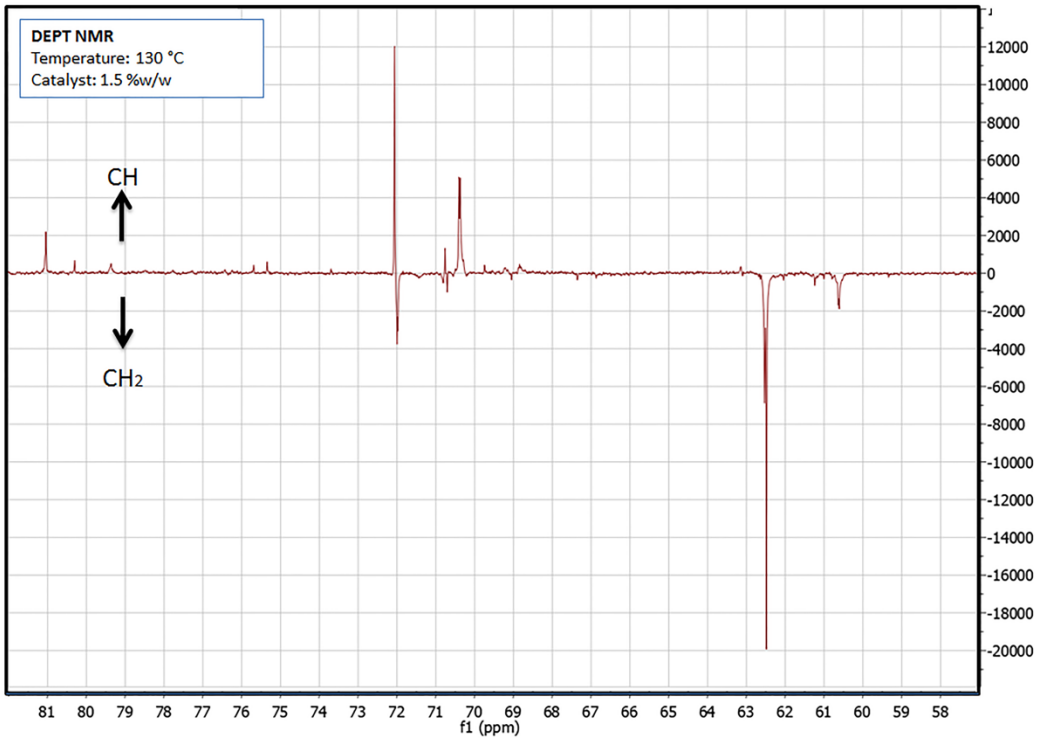


Figure 2.5 DEPT spectra of the polyglycerol synthetized at 130 °C and catalyst concentration of 1.5 w/w% (Treatment 5).

In order to study the effect of temperature and catalyst concentration on the polymer morphology, a measurement of the abundance of each peak in quantitative ^{13}C NMR spectra was made using relative integrals. Experiment results performed at 130°C, catalyst concentration of 1.5 w/w% and at 170 °C, catalyst concentration of 5.2 w/w%, respectively, are summarized in Tables 2.5 and 2.6. The analysis was performed using quantitative ^{13}C and DEPT NMR spectra.

Table 2.5 Relative integrals of quantitative ^{13}C NMR spectrum peaks of polyglycerol synthetized at 130 °C and catalyst concentration of 1.5 w/w %.

Shift (ppm)	Relative Integral	Percentage (%)
81.13 – 80.98	1	2.6274
72.29 – 71.80	10.47	27.5092
70.92 – 70.10	8.68	22.8061
62.92 – 62.21	15.05	39.5428
60.91 - 60.37	2.86	7.5145

Table 2.6 Relative integrals of quantitative ^{13}C NMR spectrum peaks of polyglycerol synthetized at 170 °C and catalyst concentration of 5.2 w/w%.

Shift (ppm)	Relative Integral	Percentage (%)
81.6 – 80.78	1	1.2621
80.19 – 79.08	2.9	3.6602
76.30 – 75.53	1.87	2.3602
75.64 – 75.05	1.79	2.2592
74.05 – 73.23	2.33	2.9408
72.79 – 71.52	15.35	19.3740
71.24 – 70.61	7.36	9.2894
70.64 – 69.83	11.96	15.0953
69.60 – 69.05	5.49	6.9292
69.05 – 68.38	6.43	8.1156
67.60 – 67.16	3.1	3.9127
67.01 – 66.72	2.24	2.8272
62.87 – 62.23	7.37	9.3020
61.24 – 60.91	2.51	3.1680
60.87 – 60.43	5.69	7.1816
59.94 – 59.61	1	1.2621
59.54 – 59.24	0.84	1.0602

Synthetized polyglycerol degree of branching depends on temperature and catalyst concentration. Polyglycerol degree of branching increases as temperature and catalyst concentration increases. The percentage of branching chains of two polyglycerols synthetized at different temperatures and catalyst concentration were compared taking into account that ^{13}C resonances in a region of 74 to 82 ppm indicate branched structures. Polyglycerol synthetized at lower temperature and amount of catalyst (130 °C, 1.5 w/w%) has 2.63% of branching chains, whereas, polyglycerol synthetized at higher temperature and amount of catalyst (170 °C, 5.2 w/w%) has 12.48%. A possible explanation of temperature effect on polyglycerol morphology is that homogeneous acid–catalyzed etherification of glycerol at elevated temperatures may proceed with the formation of glycidol, an epoxy intermediate compound, which can further react with glycerol forming branched structures, as reported in other studies [13]. The spectra region that indicates the presence of polyglycerol branched structures exhibit variety of carbon shifts, see table 6. This variety of carbon shifts could be related with electron clouds caused by the diversity of neighboring chains that may be around the –CH-O carbons in polyglycerol structure.

The presence or absence of cyclization during polymerization process could not be supported by ^{13}C NMR analysis since cyclic structures possess the same structural units as lineal or branching chains, see table 4 [20]. Presence of several peaks in a region of 62 to 72 ppm in the synthetized polyglycerol at temperature of 170 °C and catalyst concentration of 5.2 w/w%, may suggest the presence of cyclic structures, as reported in other studies [13], see table 2.6.

2.3.4 Glass transition temperature (Tg) analysis of synthetized polyglycerols

Glass transition temperature (Tg) is defined as the temperature at which polymer properties change drastically due to the internal movement of polymer chains [19]. The presence of branched chains in the polymer structure could cause two opposite effects that influence glass transition temperature [21]. First effect is the restriction of the segmental mobility due to the high number of chain

ends increasing glass transition temperature. Second effect is the increase of material free volume due to high number of chain ends that allows segmental mobility decreasing glass transition temperature (Tg). Glass transition temperature of synthetized polyglycerol at 170 °C and catalyst concentration of 5.2 w/w % is higher than the synthetized polyglycerol at 130 °C and catalyst concentration of 1.5 w/w %, varying from -47.56 °C to -52.89 °C, respectively, see figure 2.6. The differences of glass transition temperature may be cause by a decrease of polymer chains mobility of structures with higher degree of branching present in the synthetized polyglycerol at 170 °C and catalyst concentration of 5.2 w/w%. Polyglycerol is a polymer with high polar qualities conferred by terminal hydroxyl groups, which can form strong hydrogen bonding. Branched structures probably facilitate higher hydrogen bonding between terminal hydroxyl groups and consequently also contribute to increase the glass transition temperature in the synthetized polymer with higher degree of branching. Similar observations were reported previously for hyperbranched OH-functionalized aromatic polyesters [21].

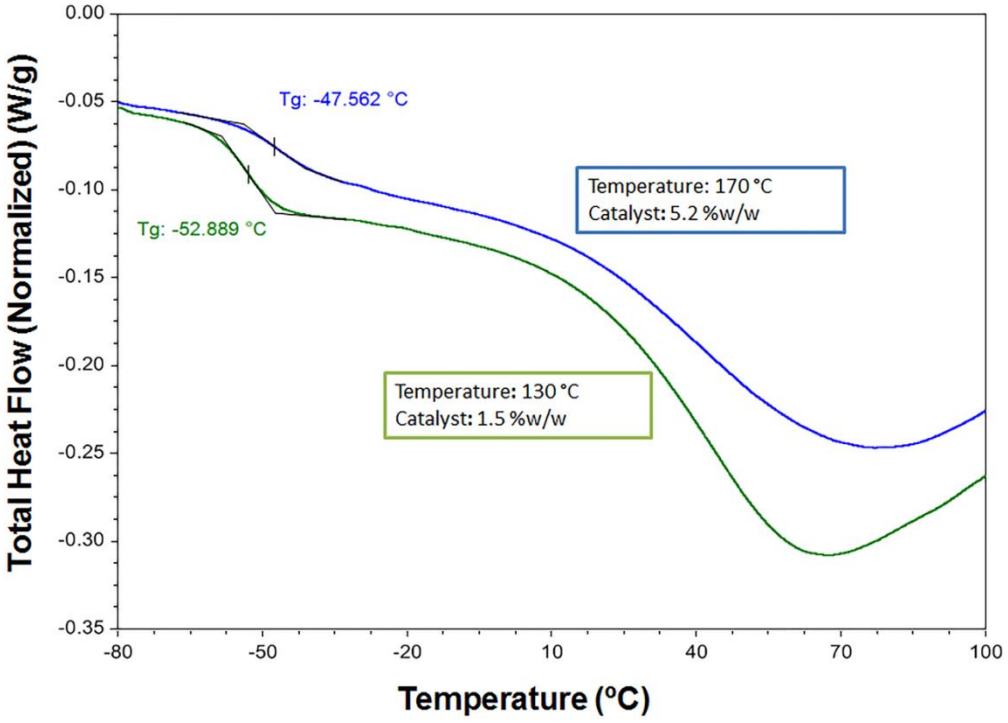


Figure 2.6 Differential scanning calorimetry analysis. The glass transition temperatures were measured for treatment with temperature: 130 °C and catalyst: 1.5 w/w% and treatment with temperature: 170 °C, catalyst: 5.2 w/w %.

2.4 Conclusions

The effects of glycerol polymerization synthesis conditions, temperature and amount of catalyst, on final polyglycerol properties were studied. It was concluded that temperature and amount of catalyst as well as the interaction between them have a significant effect on the hydroxyl number of resulting polyglycerol which determined polyglycerol functionality. FT-IR spectra analysis showed the main functional groups of polyglycerol present in all reaction products without significant differences between spectras. MALDI-TOF analysis showed that temperature and amount of catalyst have not significant effects on average molecular weight of all treatments, which exhibit Gaussian distributions and narrow polydispersities. Quantitative 13C NMR analysis showed that polyglycerol morphology is significantly affected by the synthesis conditions, temperature, amount of catalyst and the interaction between them, since structures with more branched chains

were obtained using the higher values of temperature and amount of catalyst factors tested, 170°C and 5.2 w/w% respectively. A further DSC study showed that the glass transition temperature of polyglycerol increase by increasing the amount of branched chains into the polymer structure. To conclude, it is possible to tune the morphology of glycerol- derived polyglycerol with synthesis conditions, obtaining structures with significant amount of branched chains at high levels of temperature and amount of catalyst. The change on polyglycerol morphology affects the glass transition temperature, not the average molecular weight of the resulting polymers.

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CHAPTER 3

Development of a Step-Growth Polymerization Kinetics Model for Polyglycerol Production

Abstract

A kinetic model that describes the polymerization reaction of glycerol to produce polyglycerol was developed. This model takes into account two different resistances acting in parallel; each resistance was attributed to a different phenomena. The first resistance is Arrhenius type, with constant activation energy, which is generated by the chemical reaction; whereas, the second resistance was found to correlate with the mass diffusion physical phenomenon. Polymerization reaction was monitored using thermogravimetry. Experimental data were found to properly fit the developed kinetic model. The viscosity of the reaction media increased as the polymerization reaction occurs, which caused higher physical resistance. Process variables such as: activation energy, reaction order, and a parameter of diffusion resistance were found to be temperature and heating rate independent; whereas, the frequency factor of Arrhenius equation, diffusion resistance coefficient, and a delay parameter due to inertial effect, were found to be heating rate dependent. Changes on the process variables were discussed in terms of the heating rate effect on the entropy of the reaction system.

3.1 Introduction

Recently, there have been significant governmental incentives for using biomass as a renewable alternative for fuel production [1]. The driving force for these incentives is the need to overcome the exclusive dependency on petroleum as a source of energy [2]. One of the consequences of supporting biomass as an alternative for biofuel production (bio-diesel) is the increase of crude glycerol

production, the major co-product of the transesterification reaction of vegetable oils to produce bio-diesel. Overproduction of glycerol is threatening biodiesel production as a cost effective process since it has become a waste stream that needs to be stored or converted [3]. Therefore, development of new technologies for using glycerol as a building block for value-added products may contribute to transform the actual biodiesel industry into a bio-refinery [4].

Polymerization of glycerol to produce polyglycerol, a biocompatible, biodegradable, and hydrophilic polymer, is an attractive alternative to convert glycerol into valuable materials. Polyglycerol is formed by an inert chain of polyether with abundant pendant hydroxyl groups. These pendant hydroxyl groups make polyglycerol a building block for diverse polymeric complexes [5]; for instance, polyglycerol is used as starting material for drug delivery [6] and dyes adsorption from aqueous media [7], among many other applications [8].

The understanding of polymerization kinetics of any polymer production process is an important factor to be able to tune the morphology and final physical and chemical properties of the polymer. The aim of this study is to develop a kinetic model that describes polymerization of glycerol to form polyglycerol. This model was developed based on the mathematical description of two phenomena that occur simultaneously during the polymerization: i) a chemical reaction characterized by constant activation energy and ii) a transport process that is the diffusion of reactants and by-products during the polymerization reaction. The kinetic model was fitted to experimental data obtained by thermogravimetric analysis. To our knowledge, there have not been previous reports about a kinetic model of glycerol polymerization into polyglycerol.

The process where glycerol is converted into polyglycerol by an etherification reaction is analyzed. Using the direct step-growth synthesis, it is possible to obtain a high molecular weight polymer, as recently reported by Salehpur et al [9]. Synthesis of hyperbranched polyglycerol at industrial level is produced by ring-

opening polymerization of glycidol obtaining high molecular weights with narrow distributions [10]. However, the industrial production of glycidol uses raw materials that come from non-renewable petrochemical resources. Usually, glycidol production is done by hydrolysis of an epichlorohydin epoxy group followed by dehydrochlorination of 3-chloropropane – 1, 2 diol, or by epoxidation of allyl alcohol, which are not environmentally friendly methods. Polyglycerol is also produced from glycerol carbonate, an environmentally friendly monomer; however, the molecular weight of this polymer is usually low when compared to the synthesis methods just described [11]. This chapter presents a description of the fundamentals for the proposed kinetic model, experimental methods, experimental results, estimation of kinetic model parameters, analysis of the kinetic model, and conclusions.

3.2 Model fundamentals and mathematical methods

The chemical reaction to produce polyglycerol is a condensation step-growth polymerization reaction catalyzed by sulphuric acid.

A kinetic model that describes polymerization of glycerol to produce polyglycerol taking into account two simultaneous events or resistances occurring during the polymerization reaction is proposed. The first resistance is due to the chemical reaction and the second one is due to a transport process. The chemical resistance corresponds to the inverse of the specific rate of the reaction, k_A, and the physical resistance to the inverse of the specific diffusion rate, $k_{\mathfrak{D}}$:

$$\frac{1}{R_A} = k_A = Ae^{-E_a/RT} \quad , \qquad \frac{1}{R_{\mathfrak{D}}} = k_{\mathfrak{D}} = -\mathfrak{D} \qquad (1)$$

Where A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant, T is the temperature, and $\mathfrak{D}$ is the effective diffusion coefficient.

Reactant compounds diffuse through the polymer solution along with water, a reaction by-product. As the reaction occurs, the polymer chain grows and the

diffusion of the reactants through the polymeric solution becomes more difficult due to the fact that the increase in molecular weight of the polymer chain acts as a diffusion resistance. The diffusion coefficient is a function of temperature. An empirical expression of the diffusion coefficient, similar to other empirical correlations used by Wilke and Dymond [12], is proposed in this work to fit the experimental data:

$$k_{\mathfrak{D}} = B(T - C)^s \qquad (2) \qquad \frac{1}{R_t} = \frac{1}{R_A} + \frac{1}{R_{\mathfrak{D}}} \qquad (3)$$

Where T is the reaction temperature and B, C, and s are parameters that depend on the heating rate and the transport phenomena of reactants and by-products of the reaction through the polymer solution as shown in this study.

During the polymerization reaction, the proposed chemical and physical events are happening simultaneously. Therefore, the resistances are in parallel and the total inverse resistance of the reaction process (R_t) is equal to the sum of the inverse of the chemical resistance (R_A) and the inverse of the physical resistance ($R_{\mathfrak{D}}$), see equation (3). Therefore, the proposed kinetic model for the reaction rate is described by the total resistance of the reaction process times a function of concentration, $f(C_A)$; assuming $f(C_A) = C_A^n$:

$$r_p = \frac{1}{R_t} \cdot f(C_A) = \frac{1}{R_t} \cdot C_A^n = \left(Ae^{-E_a/RT} + B(T - C)^s\right) * C_{A0}^n (1 - X_A)^n \qquad (4)$$

Where C_{A0} is the initial concentration, X_A is the fractional conversion and n the order of the reaction.

The activation energy for the chemical reaction resistance was estimated using an isoconversional approach assuming that at the beginning of the polymerization reaction the physical resistance was zero. This assumption is supported by the initial low conversion of glycerol to form polyglycerol which is reflected in the low viscosity of the reacting mass [13].

For a batch reaction system the isoconversional value is:

$$\left(\frac{dX_A}{dt}\right)_{X_{Af}} = kC_{A0}^{n-1}\left(1 - X_{Af}\right)^n \qquad (5)$$

where the reaction rate was evaluated at a specific conversion X_{Af}. Since,

$$C_{A0}^{n-1}\left(1 - X_{Af}\right)^n = constant = B \ ,$$

$$\text{then, } \left(\frac{dX_A}{dt}\right)_{X_{Af}} = kC_{A0}^{n-1}\left(1 - X_{Af}\right)^n = kB = ABe^{\left(-E_a/RT\right)}$$

Linearizing:

$$ln\left(\frac{dX_A}{dt}\right)_{X_{Af}} = \ln(AB) - \left(E_a/RT\right) \qquad (8)$$

The activation energy is estimated by calculating the slope $-E_a/R$. On the other hand, the physical resistance parameters were estimated using the Levenberg-Marquardt method [14]. The monomer conversion was obtained from thermogravimetric data using the following expression:

$$X_A = \frac{m_o - m}{m_0 - m_\infty} \qquad (9)$$

where m_o is the solution mass at the beginning of the polymerization reaction , m is the solution mass at X_A conversion, and m_∞ is the solution mass after the polymerization reaction was complete.

3.3 Experimental approach

For the polymerization reaction, glycerol (Merck) was used as monomer and sulfuric acid (Merck) as the catalyst. The monomer concentration was $13238.19\ mol\ m^{-3}$. All the experiments were performed using glycerol that has been treated for water removal.

Polymerization reaction was performed at four different heating rates: $^{dT}/_{dt} = \dot{T} = 2, 3, 5\ and\ 9\ K\ min^{-1}$, from $298{,}15\ K$ to $573{,}15\ K$, and the reaction progress was monitored using a TGA Discovery from TA Instruments, Inc. (USA), equipped with nitrogen purge gas system $(50\ cm^3\ min^{-1})$.

3.4 Results and Discussion

Variations in the heating rate caused differences in the system response, as shown in the non-isothermal thermograms of glycerol polymerization, see Figure 3.1. Thermograms show the percentage of weight loss as a function of temperature at four different heating rates. Curves have similar behavior but different initiation temperatures for the polymerization reaction. These differences are due to the system response to heating rate stimulus; at slow heating rates (2-3 K/min) the system response is faster than at higher heating rates (5-9 K/min), which might be due to inertial delay occurring at higher heating rates.

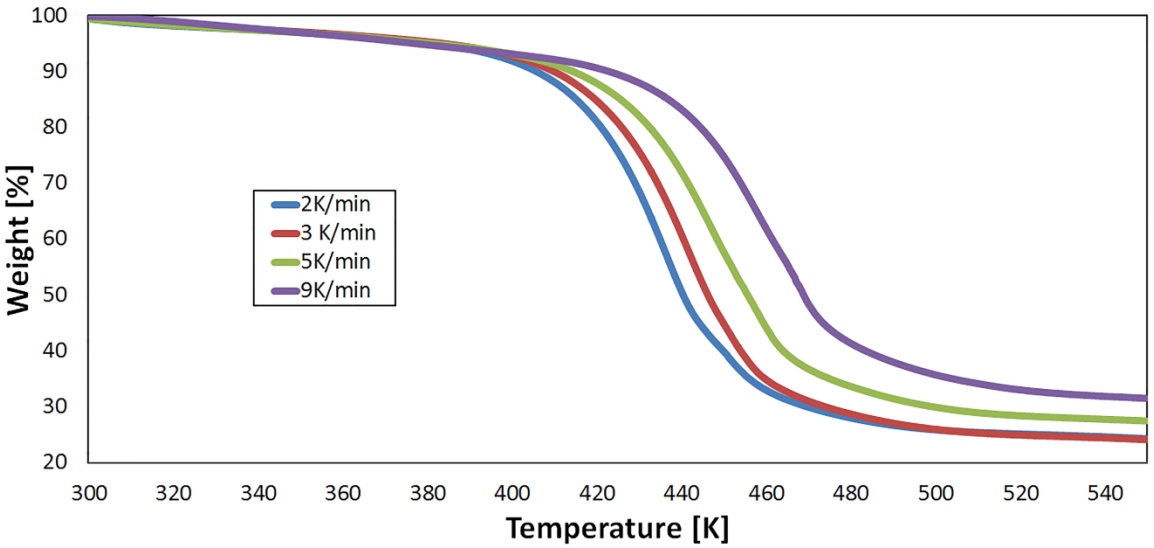

Figure 3.1 TGA non- isothermal thermograms of glycerol polymerization: percentage of loss weight as a function of temperature at four different heating rates.

Considering only the chemical reaction event during the polymerization reaction, the rate equation is given by:

$$r_p = Ae^{-E_a/RT} * C_{A0}^n (1 - X_A)^n \qquad (10)$$

Experimental data were fitted with the kinetic model described by Eq(10) using the isoconversional method described in the model fundamentals and mathematical methods section. As a result, it was found that the activation energy depends on the reaction conversion; for reaction conversions of x1, x2, x3 the activation energy were a1, a2 and a3. This result implies that the activation energy changes as a function of temperature which is against the initial assumption of Arrhenius equation. The dependence of activation energy with reaction conversions suggests the need for a change in the kinetic model to be consistent with the energy barrier concept. The proposed kinetic model considers a chemical reaction event and the diffusion process of reactants and by-products during the polymerization reaction. During the polymerization reaction, the polymer molecular weight is constantly increasing as well as the viscosity of the solution. The increase

in the solution viscosity imposes resistance against reactants and water diffusion; therefore, the proposed equation for the reaction rate that takes into account both phenomena is described below. The results of estimated kinetic parameters on Eq (4) were performed using the Levenberg-Marquardt numerical method [14] and are shown in table 3.1. Figure 3.2 shows a comparison between the reaction rates calculated with the proposed kinetic model and experimental data.

Table 3.1 Kinetic parameters obtained by Levenberg – Marquardt Method [14].

$\dot{T}$ [K/min]	Ea [J/mol]	A [1/s]	B [1/s*K^{3,5}]	C [K]	S	n	R^2
2	90000	0.331	3.3963×10^{-17}	395.19	3,5	2	0.955
3	90000	0.39	6.27×10^{-17}	403	3,5	2	0.956
5	90000	0.482	7.099×10^{-17}	407.8	3,5	2	0.959
9	90000	0.51	1.288×10^{-16}	420.2	3,5	2	0.936

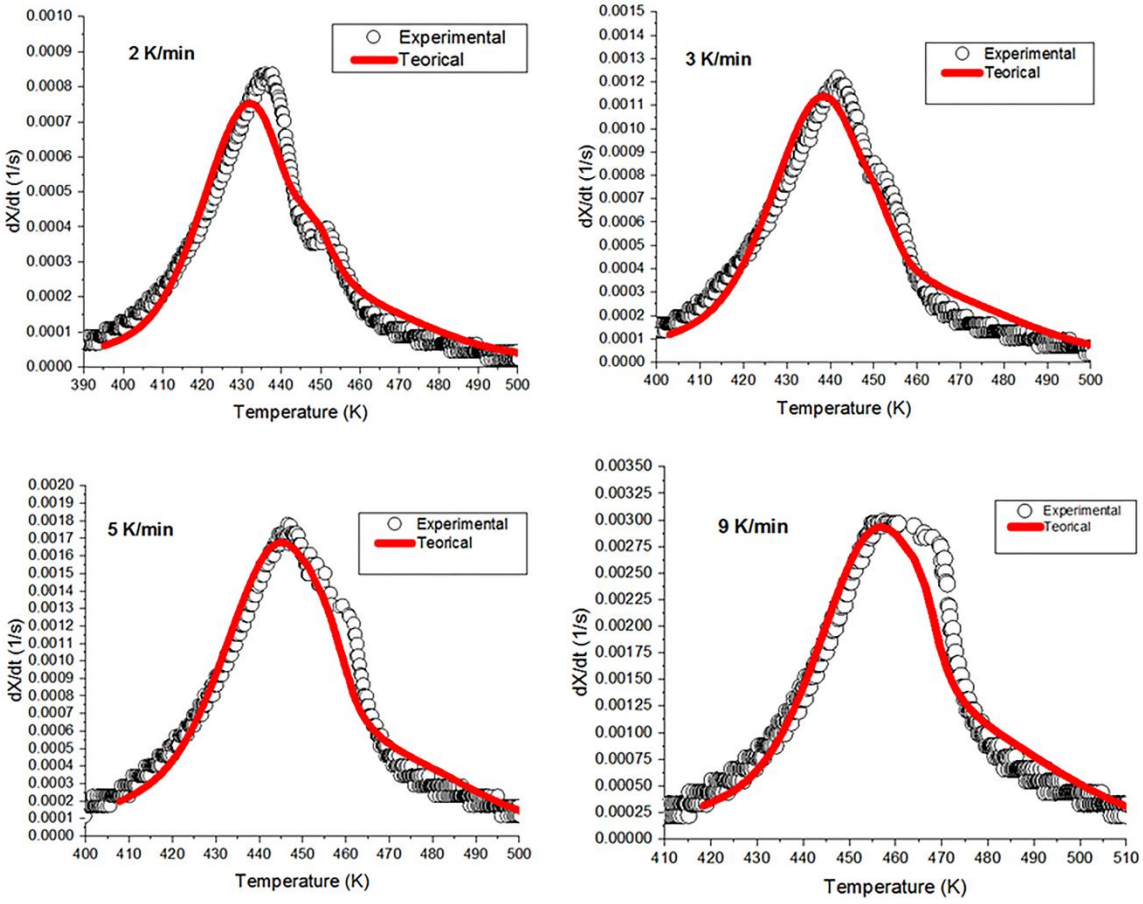

Figure 3.2 Comparison between experimental data and calculated kinetic parameters. The proposed kinetic model considers both, a chemical reaction and a diffusion event during the polymer reaction.

As mentioned before, the activation energy, E_a, was calculated by isoconversion method, assuming that at the beginning of the polymerization reaction the physical resistance is zero. The reaction order, n, and the parameter s during the convergence calculations tended to values 2 and 3.5 respectively; therefore, the reaction order and exponent s were considered non-dependent parameters of the heating rate and were fixed at 2 and 3.5, respectively. The fixed value of the reaction order is similar to other values used in similar polymerization reactions [15]. The parameter s is a solvent – solute correlation factor inherent to the reaction system; since neither the solvent, nor the solute was changed in the thermogravimetic experiments, s is a constant parameter. The only variable in the four TGA experiments was the heating rate. The variation of heating rate causes

an increment in the entropy of the system and an inertia effect that is reflected in the kinetic model. Eq(11) shows an entropy balance for the closed reacting system. The first and second terms increase with the heating rate; since the first accounts for entropy entrance due to heat transfer rate and the second for generation of entropy due to irreversibility of the process. As a result, the entropy accumulation in the system increases with the heating rate:

$$\frac{\delta \dot{Q}}{T} + \dot{S}_g = \frac{dS}{dt} \qquad (11)$$

In addition to the increment of entropy in the system, there is an inertial effect as the heating rate increases which causes a retarded response of the system.

The increment of entropy in the system and the inertial effect are reflected in the parameters A, B and C of the kinetic model. The pre-exponential factor A, which depends on the frequency of particle collision increases drastically and then becomes almost constant with an increase of the heating rate above 3 K/min, table 3.1. This behavior can be explained in terms of accumulation of entropy in the system. As the heating rate increases, there is an increase of disorder in the system, which results in increasing the frequency of particle collisions until a saturation point where the pre-exponential factor slightly changes with the heating rate. The factor B of the physical resistance term is related to the diffusion resistance of the reactants and by-products through the polymer solution during the reaction. It is expected that an increase of heating rate which causes an increase of disorder in the system, difficult the diffusion of reactants and byproducts though the system. Thus, factor B increases with the heating rate (Table 3.1). Finally, the parameter C, which represents the inertia effect that the system experiences with an increase of heating rate, increases with the heating rate. The polymerization process starts later at higher heating rates (Figure 3.1), since the system has no time for an instantaneous response because of its own inertia. As a result, the reaction starts at higher temperatures, see table 1. The behavior of physical and chemical resistances during the polymerization reaction was studied. Figure 3.3a

shows the calculated chemical and physical resistances at a heating rate of $9\ K/min$. As expected, at the beginning of the polymerization process the chemical resistance has higher values than the physical resistance until a specific temperature, where the physical resistance becomes greater. This behavior is consistent with the initial hypothesis which states that chemical resistance has predominance at the beginning of polymerization process because the reaction system has low viscosity; however, as the conversion from glycerol to polyglycerol increases the viscosity of the polymer solution increases becoming more relevant the effect of the physical resistance until a specific temperature is reached (approximately 450 K) where this resistance becomes greater than the chemical one. The molecular weight distribution of the synthesized polymer with heating rate of $9\ K/min$ and at 453K was measured using MALDI-TOF MS. The resulted polymer molecular weight distribution is distributed between 2500 to 4000 Da, see figure 3.3b. Similar molecular weight distribution of polyglycerol has been reported [9]. This calculations suggests that at temperatures below the temperature where the physical resistance becomes greater than the chemical resistance, polyglycerol has been synthesized. It is possible that when the physical resistance becomes greater than the chemical resistance a polymer degradation occurs. This hypothesis will be study in future works.

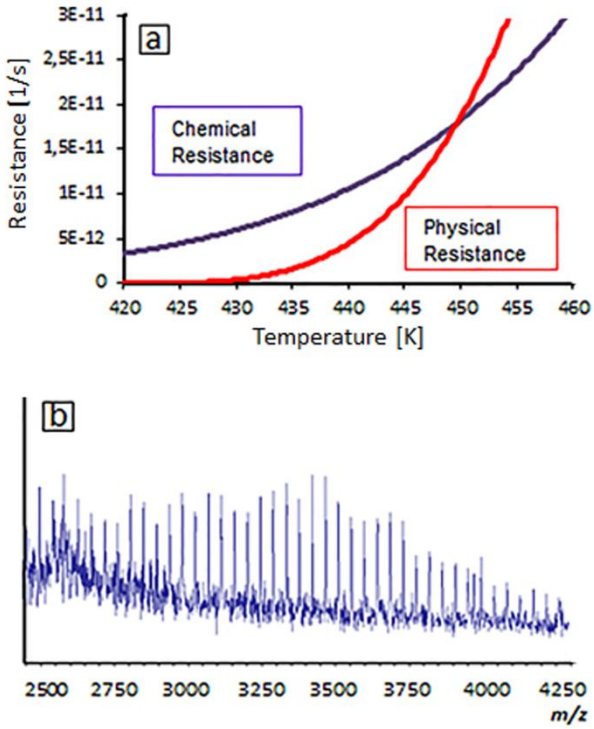

Figure 3.3 (a) Calculated chemical and physical resistances with a heating rate of 9 K/min. At the beginning of the polymerization process the chemical resistance has higher values than the physical resistance; until a specific temperature, where the physical resistance becomes greater. (b) MALDI-TOF MS spectra of polyglycerol by taking a sample at 453 K for the reaction of 9 K/min.

3.5 Conclusions

A kinetic model that describes the polymerization of glycerol to polyglycerol was successfully developed. The proposed kinetic model is based on a mathematical description of two phenomena that occur simultaneously during the polymerization reaction: a chemical reaction characterized by constant activation energy and a transport process, the diffusion of reactants and co-products during the polymerization reaction. The results showed that the chemical resistance has predominance at the beginning of polymerization reaction because the reaction system has low viscosity; however, as the conversion of glycerol to polyglycerol increases the viscosity of the polymer solution increases becoming more relevant the effect of the physical resistance until a specific temperature is reached, where

this resistance becomes greater than the chemical one. The kinetic model parameters depend on the system entropy accumulation and an inertia effect caused by the increase of heating rate. Finally, the chemical resistance prevails at lower conversion and the physical resistance at high conversion. The breaking point of conversion increases as the heating rate increases.

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CHAPTER 4

Synthesis and Characterization of Novel Stimuli-Responsive Hydrogels Based on Polyglycerol

Abstract

Temperature and pH responsive hydrogels from the crosslinking between glycerol-derived polyglycerol and biodegradable acids –citric and oleic acids- were successfully synthesized. The differences between functional groups between polyglycerol and polyglycerol-derived hydrogels were determined by FTIR spectroscopy. The swelling behavior and mechanism of synthesized hydrogels were studied. The hydrogels swelling capability varies at 4, 5 7 and 10 pH values as well as at 25, 35, 55 and 85 °C. The hydrogel response to pH changes is related to functional groups in its structure. The temperature response of hydrogel is related to its glass transition temperatures, measured by DSC analysis. TGA analysis showed the degradation behavior of synthesized materials. Morphological study was performed by Scanning Electron Microscopy (SEM). Final product of this study is an environmentally friendly hydrogel that absorbs 13.7 times its own weight.

4.1 Introduction

Hydrogels are polymeric cross-linked, hydrophilic, three – dimensional networks that are not soluble in water but can absorb large quantities of this molecule [1, 2]. Due to their swelling ability, hydrogels have been studied extensively for a variety of applications such as drug delivery [3-6], removal of impurities in aqueous solutions [7, 8], biosensors [9] and spectrophotometric determination of drugs [10]. Hydrogels can be made of synthetic or natural monomers. Commercial hydrogels have been conventionally synthesized from

toxic acrylates and acrylamides [11]. Hydrogels based on renewable materials are of interest as a consequence of their environmental- friendly character, non-toxic nature and biodegradability [12, 13]. The aim of this work is to synthetize and characterizes a novel hydrogel from biodegradable monomers such as glycerol, citric and oleic acids.

Glycerol is a bio-based monomer candidate for sustainable polymeric complexes production, which give to this co-product of the transesterification of vegetable oils a higher added value [14]. The glycerol polymerization product, polyglycerol, can be used as a building block for hydrogels synthesis that may contribute to transform the actual biodiesel industry into a bio-refinery [15]. However, polyglycerols are traditionally synthesized by ring – opening polymerization of glycidol, a toxic monomer [16, 17]. Recently, Salehpour and Zulliani [18] synthesized hydrogels by crosslinking the glycerol-derived polyglycerol with another polymer, the poly (ethylene glycol) diglycidyl ether PEGDE. The resulting hydrogels exhibited pH-dependent swelling behavior with a higher swelling capability at acidic pH value, compared with swelling at neutral and basic pH values.

The present study is focus in the development of a novel polymeric material and understanding its structure-properties relation. The novel material is synthetized crosslinking the glycerol-derived polyglycerol with biodegradable acids such as citric and oleic acids. Citric acid is a multifunctional monomer with pendant functional groups that allow future ester bond-crosslink and hydrogen bonding [19, 20]. Previous studies have reported citric acid-contained hydrogels used as a crosslink agent; for instance, with poly(vinyl alcohol) [21] and cellulose [22]. Oleic acid is a biocompatible and biodegradable fatty acid. The presence of a carboxyl group and the possible acid-catalyzed hydration of oleic acid double carbon-carbon bond allow crosslinks by esterification and etherification reactions, respectively. This fatty acid has been traditionally used to improve mechanical properties and chemical resistance in polymer materials [23, 24]. A second crosslink agent, oleic

acid, is used to tune the mechanical behavior of polyglycerol–based hydrogels cross-linked with citric acid.

An experimental design was performed to study the effect of cross-linked agent concentration, ratio between citric and oleic acid, and the functional groups present in these biodegradable acids on final hydrogel morphology, absorption capability, and thermal properties. Additionally, temperature and pH stimuli-response of hydrogels were evaluated. The synthetized hydrogels were characterized using Scanning Electron Microscopy (SEM), Differential Scanning Calorimetric (DSC), Thermogravimetric Analysis (TGA) and Fourier Transform Infrared Spectroscopy (FTIR). The final product of this study is an environmentally friendly hydrogel that absorbs 13.7 times its own weight and changes its swelling capability responding to changes in temperature and pH.

4.2 Experimental

4.2.1 Materials

Glycerol (85%) and Sulfuric acid (95%) were obtained from Merck. Citric acid (99%) is a commercial product of Suquin Ltda., Bucaramanga, Colombia; Oleic acid used in this study was purchased from the local market. Its composition is listed in table 4.1.

Table 4.1 Composition of oleic acid. Characterization was made using a gas chromatography system (Agilent Technologies 6890 series), coupled to a FID detector, using an Agilent DB23 column and SUPELCO 38 FAMES as standards.

Fatty Acid	**Oleic Acid Area Percentage %**
Palmitic (C16:0)	9.0828
Stearic (C18:0)	8.1245
Oleic (C18:1n9c)	32.1425
Linoleic (C18:2n6c)	36.3093
Linolenic (C18:3n3)	3.5647
Eicosenoic (C20:1)	4.0572
Others	6.719

4.2.2 Experimental procedure

4.2.2.1 Glycerol polymerization

Glycerol polymerization was carried out in a 50 mL glass reactor equipped with a nitrogen inlet, catalyst feeding, thermometer inlet, and a distillation trap to continuously remove water from the reaction mixture. Temperature was maintained at 160 ℃ using a temperature-controlled heating bath. A vacuum pump was attached to the reactor through the condenser; while, condensation reactions were carried out at pressures below 22 kPa until hydrogel product reached the gel point. Sulfuric acid was used as catalyst in an amount of 4.8% w/w.

4.2.2.2 Polyglycerol Crosslinking

The crosslinking agents –citric and oleic acids – were added to the reaction mass of glycerol polymerization, just before this reach the gel point, without further addition of catalyst. The reaction proceeded until the hydrogel reached the gel point. An experimental design was performed to establish the effect of the content of cross-linked agent as well as the ratio between citric and oleic acid on hydrogels absorption capability. Five different molar ratios 1:2, 1:1.15, 1:1, 1:0.5 and 1:0.05, between hydroxyl groups of polyglycerol (PG) and carboxyl groups of crosslinking agents (CG) , citric and oleic acids (molar ratio *OH:COOH*), were established. For each mentioned ratio between hydroxyl and carboxyl groups, three different molar ratios were established between citric acid (CA) and oleic acid (OA), *citric acid: oleic acid*, as follows: 90:10, 70:30 and 50:50 % mol, see table 4.2. A total of fifteen experiments were randomized and two replicates of each were performed. After polymerization and crosslinking process, a washing with distilled water was performed to remove the catalyst and unreacted monomers.

Table 4.2 Experimental design layout. Five different molar ratios were established between hydroxyl groups of polyglycerol (PG) and carboxyl groups of crosslinking agents (CG). In turn, three different molar ratios were established between the crosslinking agents

Molar ratios of hydroxyl groups of polyglycerol (PG) and carboxyl groups of crosslinking agents (CG)	**Molar ratios between citric acid (CA) and oleic acid (OA)**		
	90:10	70:30	50:50
1:2	PG1:CG2 (90%CA-10%OA)	PG1:CG2 (70%CA-30%OA)	PG1:CG2 (50%CA-50%OA)
1.5	PG1:CG1.5 (90%CA-10%OA)	PG1:CG1.5 (70%CA-30%OA)	PG1:CG1.5 (50%CA-50%OA)
1:1	PG1:CG1 (90%CA-10%OA)	PG1:CG1 (70%CA-30%OA)	PG1:CG1 (50%CA-50%OA)
1:0.5	PG1:CG0.5 (90%CA-10%OA)	PG1:CG0.5 (70%CA-30%OA)	PG1:CG0.5 (50%CA-50%OA)
1:0.05	PG1:CG0.05 (90%CA-10%OA)	PG1:CG0.05 (70%CA-30%OA)	PG1:CG0.05 (50%CA-50%OA)

4.2.3 Characterization

Absorption tests were carried out (equation 1) to establish the swelling capability of synthesized hydrogels at room conditions [18]. In order to establish if the synthesized hydrogels have response to external stimuli, absorption measurements were made at temperatures of 35°C, 55°C and 85°C. Furthermore, absorption measurements were made in *Hanna Instruments* buffer solutions of pH 4,01 ±0,01, pH 7,01 ±0,01 and pH 10,01 ±0,01. All measurements were done by duplicate.

$$\%S = \frac{Wn - Ws}{Ws} * 100\% \quad \textbf{(1)}$$

Where Wd is the weight of dry hydrogel and Ws is the weight of swollen hydrogel. Fourier transform infrared Spectroscopy (FTIR) was used to identify functional groups in synthesized hydrogels. The infrared spectra were obtained in transmittance mode in a Thermo Scientific spectrometer (Nicolet 1550 FT-IR). Differential Scanning Calorimetry (DSC) measurements were carried out in a Differential Scanning Calorimeter Discovery, TA Instruments, Inc. (USA), modulated DSC experiment. Modulated amplitude temperature was 1 ° C, a period of 60 seconds in a temperature range of -10°C to 300 °C at a heating rate of 3°C/min and nitrogen purge gas (50 mL/min). Thermogravimetric analysis (TGA) was done in a range of temperature from 25 to 500℃ with a heating rate of 5 °C/min using a TGA Discovery from TA Instruments, Inc. (USA), equipped with nitrogen purge gas system (50 mL/min). Before Scanning Electron Microscopy (SEM) measurements for morphology of synthesized hydrogels, samples were fully swollen in distilled water then frozen in liquid nitrogen and lyophilized for 72 h. Freeze – dried hydrogels were consequently fractured for interior morphology visualization. The uncoated environmental SEM images were taken using a Quanta FEG 650 at acceleration voltages of 15 Kv.

4.3 Results and discussion

4.3.1 Hydrogel Synthesis

Hydrogels were synthetized by reacting glycerol-derived polyglycerol with citric and oleic acids crosslinking agents, see Figure 4.1. Crosslinked network was obtained by following different possible chemical reactions. Two different chemical reactions between polyglycerol hydroxyl groups and citric acid functional groups, and two different chemical reactions with oleic acid functional groups. With citric acid, polyglycerol hydroxyl groups can react with three carboxylic groups present in this acid by esterification reactions and with the hydroxyl group by an etherification reaction. With oleic acid, polyglycerol hydroxyl groups can react with the carboxylic

group by an esterification reaction, and with the hydrated carbon-carbon double bonds of this acid.

Fifteen experiments were established in the experimental design. However, only in ten experiments was possible to obtain crosslinked networks. The concentration of oleic acid was a crucial factor to obtain hydrogels. At high concentration of oleic acid there is poor crosslinking efficiency.

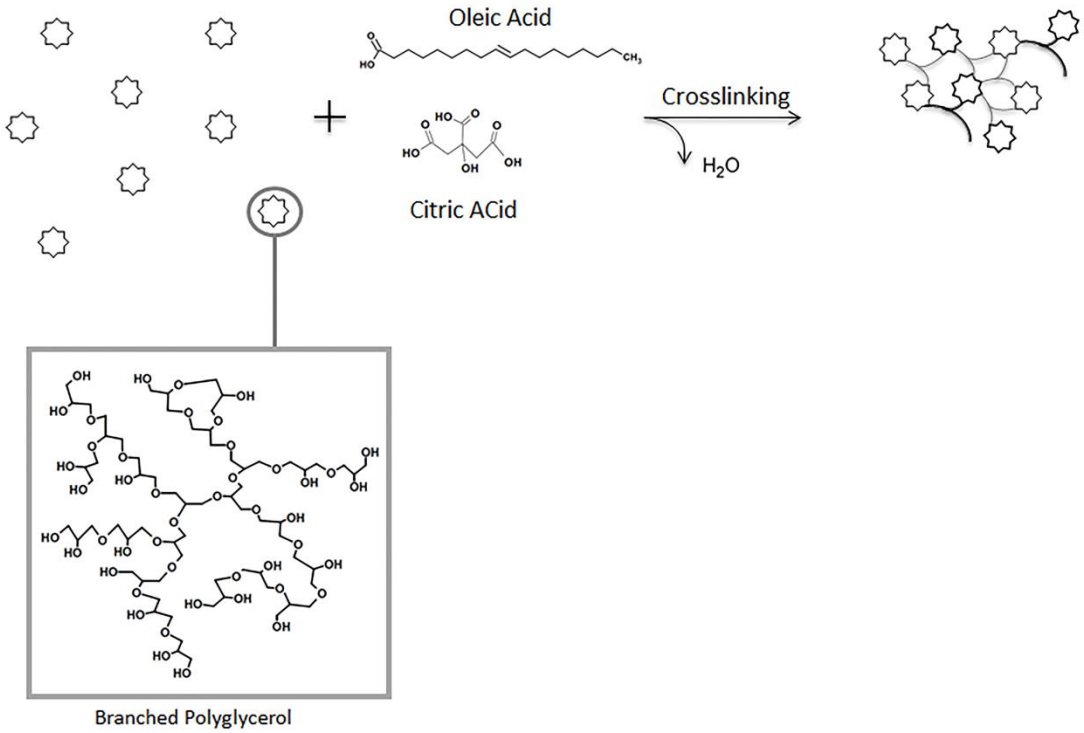

Figure 4.1 Schematic representation of the polyglycerol crosslinking reaction with citric and oleic acids. The depicted polymer structure shows just a fragment of the polymer [25, 26].

4.3.2 FTIR results

FTIR was carried out to identify synthetized hydrogels functional groups and compare them with polyglycerol spectra, see Fig. 4.2. The hydrogel and

polyglycerol spectra show hydroxyl group band from 3600 to 3100 cm^{-1} indicative of hydrogen bonded alcohol groups and alkyl stretching bands from 3000 to 2800 cm^{-1} [27]. Hydrogel O-H stretch presents a loss of intensity with respect to the same polyglycerol band as a consequence of crosslinking linkages. Absorptions at 1100–1000 cm^{-1} are related to stretching of the ether groups that forms the polyglycerol backbone [18]. Finally, absorption at 1730 cm^{-1} in hydrogel spectrum is related to the carbonyl stretch C=O of aliphatic esters due to crosslinking linkages.

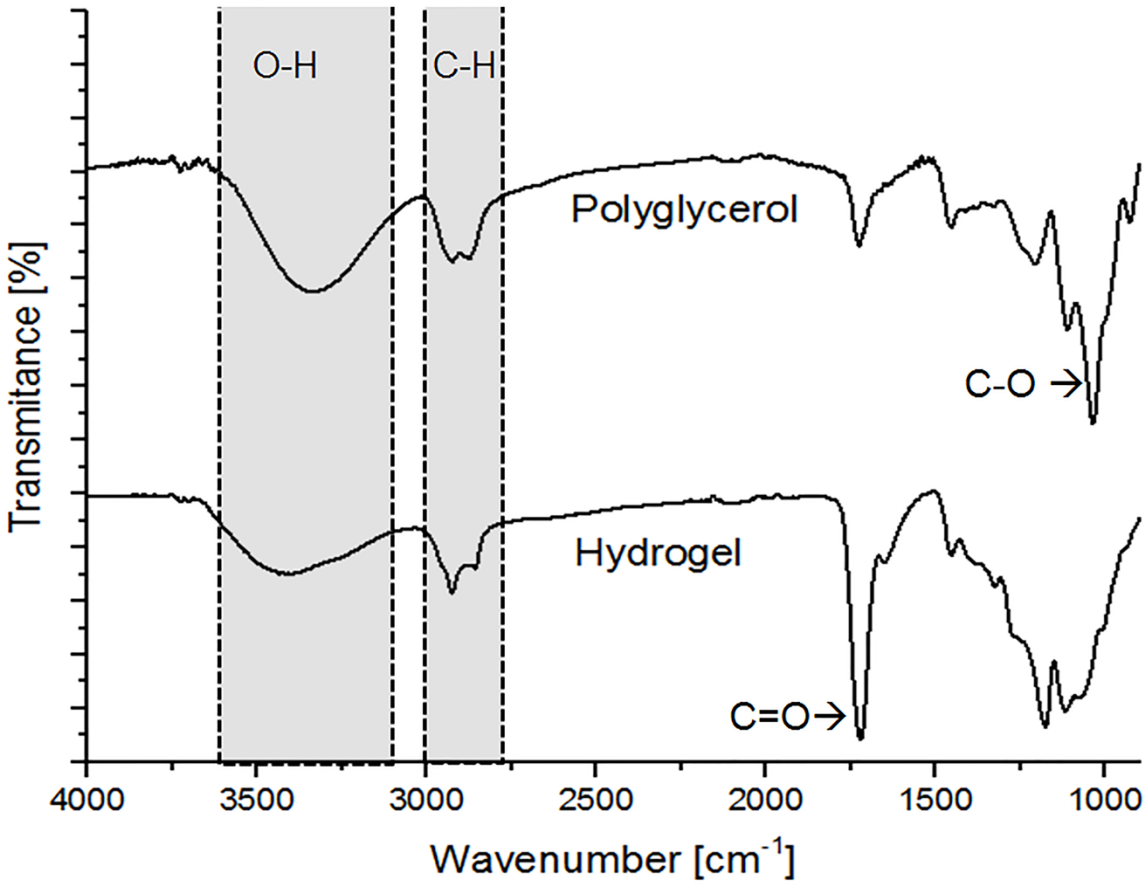

Figure 4.2 FTIR spectra of glycerol – derived polyglycerol and polyglycerol hydrogel. The main peaks associated with the structures are highlighted.

4.3.3 Swelling properties

The synthesized hydrogels were tested to determinate their swelling behavior as a function of time in aqueous solution, according to eq. 1. Hydrogels swelling capability is significantly affected by the content of cross-linked agent as well as the ratio between citric and oleic acid, see Figure 4.3. The hydrogels swelling ability decrease with the increase of oleic acid content. Possible explanations of this behavior are the cross-linker hydrophobic nature conferred by hydrocarbon chains of oleic acid [28] and high degree of crosslinking that reduces free volumes inside the network available to retain water molecules, see Figure 4.3B.

The hydrogel with higher swelling, the treatment with a molar ratio between hydroxyl groups of polyglycerol and carboxyl groups of crosslinking agents of 1:0.5 and a molar ratio between citric and oleic acids of 90%-10% -PG1:CG0.5 (90% CA -10% OA)-, absorbs more than 7 times its own weight. Probably, this swelling behavior is related to the affinity with water of the abundant hydroxyl groups attached to the hydrogel backbone since theoretically only half of these end groups reacted to form the crosslinking linkages, see Figure 4.3A. Furthermore, the crosslinks between network chains are enough to avoid polymer dissolution and at the same time, they present free volumes that are available to allow water molecules to penetrate within the hydrogel network. The swelling behavior of this hydrogel is similar to the previously reported hydrogel based on the glycerol – derived polyglycerol crosslinking with PEDGE [18]. However, in this work were used biodegradable non-polymeric materials as crosslinking agents.

In addition, the treatment with a molar ratio between hydroxyl groups of polyglycerol and carboxyl groups of crosslinking agents of 1:1.5 and a molar ratio between citric and oleic acids of 90%-10% -PG1:CG1.5 (90% CA -10% OA) absorbs more than 6 times its own weight (Figure 3A). Contrary with the above mentioned treatment –PG1:CG0.5 (90% CA -10% OA)-, this hydrogel exhibits a high crosslinking level. A probably explanation is that in this case, a reaction between some hydroxyl groups of citric acid was carried out. As a consequence,

the crosslinking chains increased their length and the cross-linked network has more capability to hold water molecules.

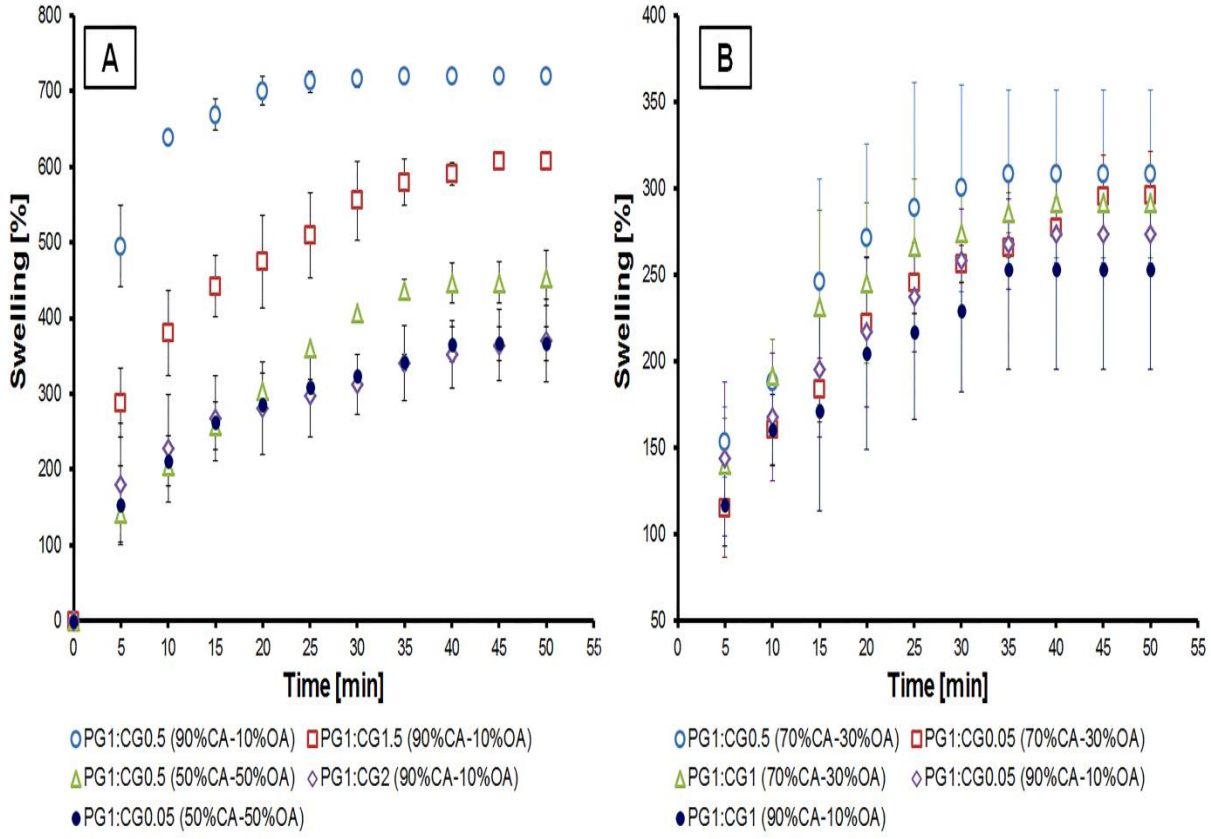

Figure 4.3 Swelling behaviors of synthesized hydrogels, measured at 25°C and a pH value of 5. Swelling percent was calculated using Eq. (1).

4.3.3.1 Swelling Kinetics

To study the mechanism of water molecules diffusion within the synthesized hydrogel, water absorption as a function of time –see Fig. 4.3- were fit to the phenomenological Fick law described by the equation:

$$Q(t) = Kt^n \quad \textbf{(2)}$$

Where *Q (t)* refers to the tested swelling ratio at time *t*, *k* is the swelling rate front factor, and *n* is the kinetic exponent. The exponent *n* is related to the type of absorption mechanism of hydrogels. If *n* is equal to 0.5 indicates Fickian diffusion which is related to a solvent diffusion rate slower than polymer relaxation. If *n* is equivalent to 1 the diffusion is non-Fickian, the diffusion process is faster than the polymer relaxation rate. Values of n between 0.5 and 1 indicate non- Fickian diffusion where diffusion and relaxation rates are comparable [29]. Values of n below 0.5 indicate Fickian diffusion known as "Less Fickian" behavior [30]. The synthetized hydrogels have *n* values lower than 0.5 showing that water diffusion rate is slower than polymer relaxation, see table 4.3. Treatment with a molar ratio between hydroxyl groups of polyglycerol and carboxyl groups of crosslinking agents of 1:0.5 and a molar ratio between citric and oleic acids of 50%-50% -PG1:CG0.5 (50%CA-50%OA) – has the higher *n* value of all synthetized hydrogels. We hypothesize that the specific cross-linked agent concentration and ratio between citric and oleic acid of this treatment allow a crosslinking with short crosslinking chains –there is not enough citric acid to allow reaction between some of its hydroxyl groups – that are surrounded by a significant quantity of hydrophobic chains of oleic acid. Consequently, the relaxation of macromolecular chains will be slightly lower going from a "less Fickian" process to a practically Fickian process.

The treatment with a molar ratio between hydroxyl groups of polyglycerol and carboxyl groups of crosslinking agents of 1:0.5 and a molar ratio between citric and oleic acids of 90%-10% -PG1:CG0.5 (90%CA-10%OA)- has the lowest *n* value of all synthetized hydrogels. Probably, three factors are related with this behavior: the partial crosslinking, the abundant pendant hydroxyl groups and the small amount of oleic acid. This results in an increase in diffusion of water molecules into the hydrogel network [28].

Table 4.3 Swelling parameters of polyglycerol derived hydrogels.

Treatment	Fick Coefficients		Swelling Equilibrium
	n	K	(%)
PG1:CG0.5 (90%CA-10%OA)	0.1297	0.62855	720.4046
PG1:CG1.5 (90%CA-10%OA)	0.3132	0.30561	606.801
PG1:CG0.5 (50%CA-50%OA)	0.4991	0.15255	453.653
PG1:CG2 (90%CA-10%OA)	0.30812	0.30251	370.493
PG1:CG0.05 (50%CA-50%OA)	0.35431	0.26258	366.708
PG1:CG0.5 (70%CA-30%OA)	0.28783	0.34799	308.465
PG1:CG0.05 (70%CA-30%OA)	0.39406	0.22148	295.855
PG1:CG1 (70%CA-30%OA)	0.28579	0.34653	291.805
PG1:CG0.05 (90%CA-10%OA)	0.30444	0.31942	273.915
PG1:CG1 (90%CA-10%OA)	0.3308	0.29001	253.59

4.3.3.2 Effect of pH on swelling behavior

The synthetized hydrogel with higher swelling capability at pH 5 reported in last section was selected to study the influence of pH on water absorption. This hydrogel has a molar ratio between citric and oleic acids of 90%-10% -PG1:CG0.5 (90% CA -10% OA)-. The hydrogel swelling behavior was studied at pH of 4, 5, 7, and 10. From the results it is concluded the hydrogel swelling behavior depended on external pH, see figure 4.4. The greater hydrogel swelling capability is observed when pH value is 10, in which the hydrogel absorbs more than 13.5 times its own weight. At pH value of 7 and 4 the hydrogel also increases its swelling capability absorbing 10 and 8.6 their own weights respectively. A possibly explanation to these results is that at pH values higher than 6, the ester linkages and unreacted carboxylic groups become ionized producing an electrostatic repulsion between polymer chains. This electrostatic repulsion increases the free volumes in hydrogel network, as reported in other studies [31]. With regards to swelling behavior at pH value of 4, is observed that hydrogel absorbs almost 9 times its own weight. At

slight acidic pH values, the ether linkages and hydroxyl groups exhibit an ionic repulsion with H^+ ions, which could result also in the increase of free volumes on hydrogel network [18].

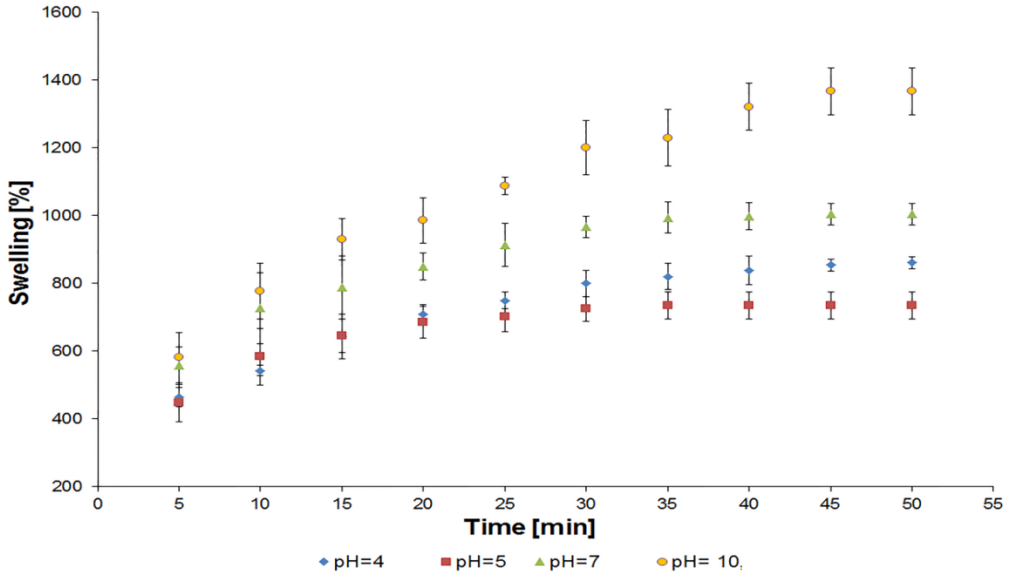

Figure 4.4 pH-dependent swelling behavior of synthesized hydrogel, measured at 25°C. Swelling percent was calculated using Eq. (1).

4.3.3.3 Effect of temperature on swelling behavior

The synthetized hydrogel with higher swelling capability at pH 5 was also selected to study the influence of temperature on water absorption. The hydrogel swelling behavior was studied at 25, 35, 55 and 85 °C. The results showed that hydrogel swelling capability depend on external temperature. The greater hydrogel swelling capability is observed at 85°C where the hydrogel absorbs water 8.5 times its own weight. At temperatures of 55 and 25 °C the hydrogel swelling capability is similar, more than 7 times its own weight, and at 35 °C the hydrogel absorbs water 5 times its own weight, see figure 4.5. The results can be related to the hydrogel glass transition temperature. As will be shown in next section, this hydrogel present two glass transition temperatures. At 85°C the temperature is greater than the material glass transitions; therefore, the polymer chains have high mobility allowing easily water diffusion which result in high swelling capability. At 35°C and 55°C

hydrogen swelling capability is lower than at room temperature. These temperatures are between the glass transitions temperatures that are present in hydrogel, 28.9 and 81.5 °C. A possible explanation of this behavior is the presence of an immiscible cross-linked phase with oleic acid [32]. As Ganji *et al.* [29] explained, when glass transition is below the temperature of swelling test, the polymer chains have high mobility; contrary, when glass transition is above the temperature of swelling test, the polymer chains are not adequately mobile. In this specific case, as the temperatures of swelling tests are between the glass transitions that are present in hydrogel, the material at those temperature is formed by chains with high mobility and chains in a rubbery state –of the cross-linked with oleic acid phase- that hinder water diffusion through the network.

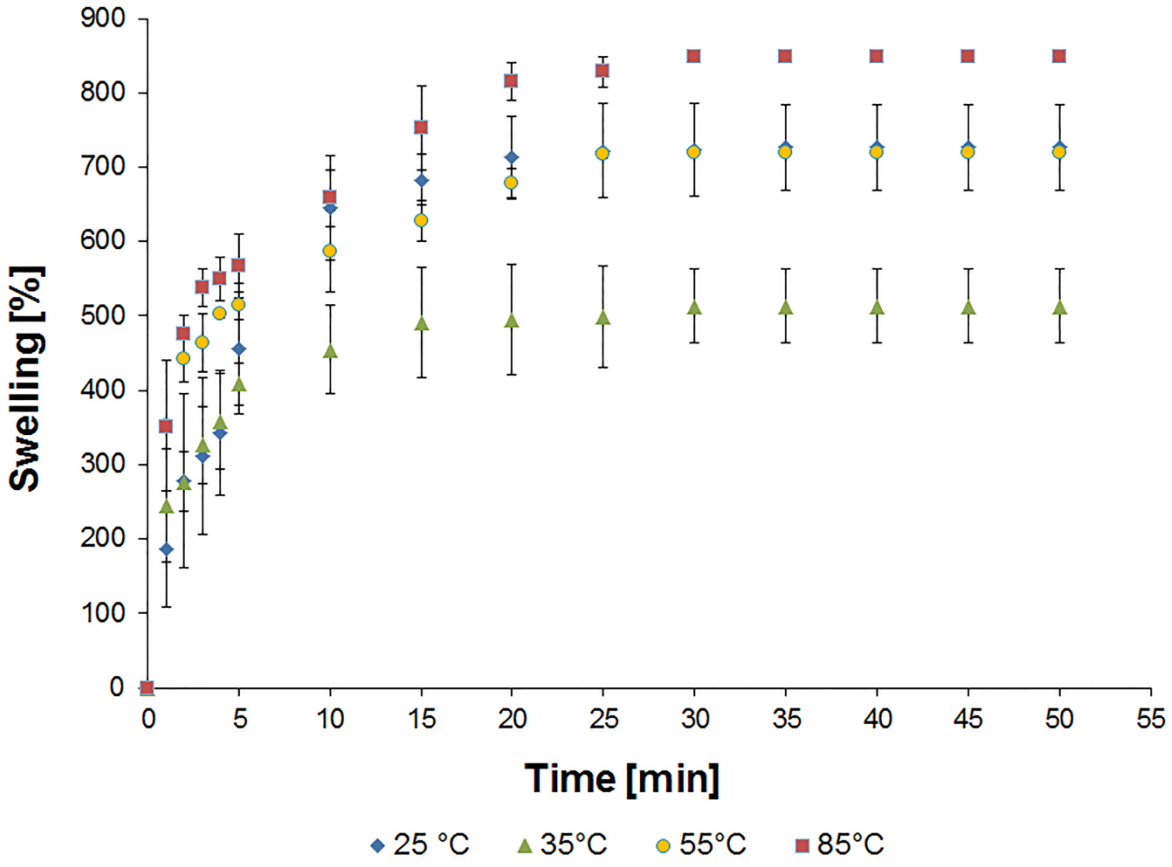

Figure 4.5 Temperature-dependent swelling behavior of synthesized hydrogel, measured at a pH value of 5. Swelling percent was calculated using Eq. (1).

4.3.4. Thermal properties

4.3.4.1 Glass transition temperatures measurement

Glass transition temperatures were evaluated using Temperature Modulated DSC technique, see Fig. 4.6. It was found that the hydrogel with more swelling capability, treatment a molar ratio between citric and oleic acids of 90%-10% -PG1:CG0.5 (90% CA -10% OA)-, shown in Figure 4.6a, presents two different glass transition temperatures. It has been reported that the number of glass transition temperatures in a polymer material is related to the number of phases that it exhibits [12]. According to this conclusion, it is suggested that synthetized hydrogel exhibits two immiscible phases, one formed by the crosslinking between polyglycerol and citric acid, and other by the crosslinking between polyglycerol and oleic acid. It is probable that due to the small quantity of oleic acid in this hydrogel, the hydrogen bonding interactions between the abundant hydroxyl groups attached to the hydrogel backbone and the hydroxyl groups of citric acid arise more easily. Consequently, the small quantity of non-interacting hydrocarbon chains of oleic acid could not be mixed, forming a separate phase [33].

Previous studies had reported glass transition temperatures of crosslinking polymers using glycerol and citric acid at 83°C [34]. Base on this report, it is suggested that the higher hydrogel glass transition is related to polyglycerol crosslinking with citric acid. Other synthetized hydrogels exhibit a single glass transition temperature, for instance treatments PG1:CG1(90%CA-10%OA) and PG1:CG0.5 (50%CA-50%OA) suggesting formation of a single phase in the hydrogel, see figures 4.6b and 4.6c. Probably, these materials – they have a higher oleic acid quantity compared with the above mentioned treatment- are conformed by a single phase due to the introduction of more quantity of non- interacting hydrocarbon chains that reduces the OH-OH interactions and allows better miscibility between two polymer phases. Likewise, the increase of glass transition temperature from 68.35°C to 80.872°C where the crosslinking goes from PG1:CG1(90%CA-10%OA) to PG1:CG0.5 (50%CA-50%OA) could be also related

to decreasing hydrogen bonding interactions between hydroxyl groups (OH-OH) due to the introduction of more non-interacting hydrocarbon chains of oleic acid between them in treatment with molar ratio between citric and oleic acids of 90%-10%- PG1:CG1(90%CA-10%OA)- [33]. From these results it can be conclude that thermal properties as glass transition, is depended on material composition. The variation of citric and oleic acids quantities provide or inhibit the interactions that lead to the formation of one or two phases in the synthesized hydrogels.

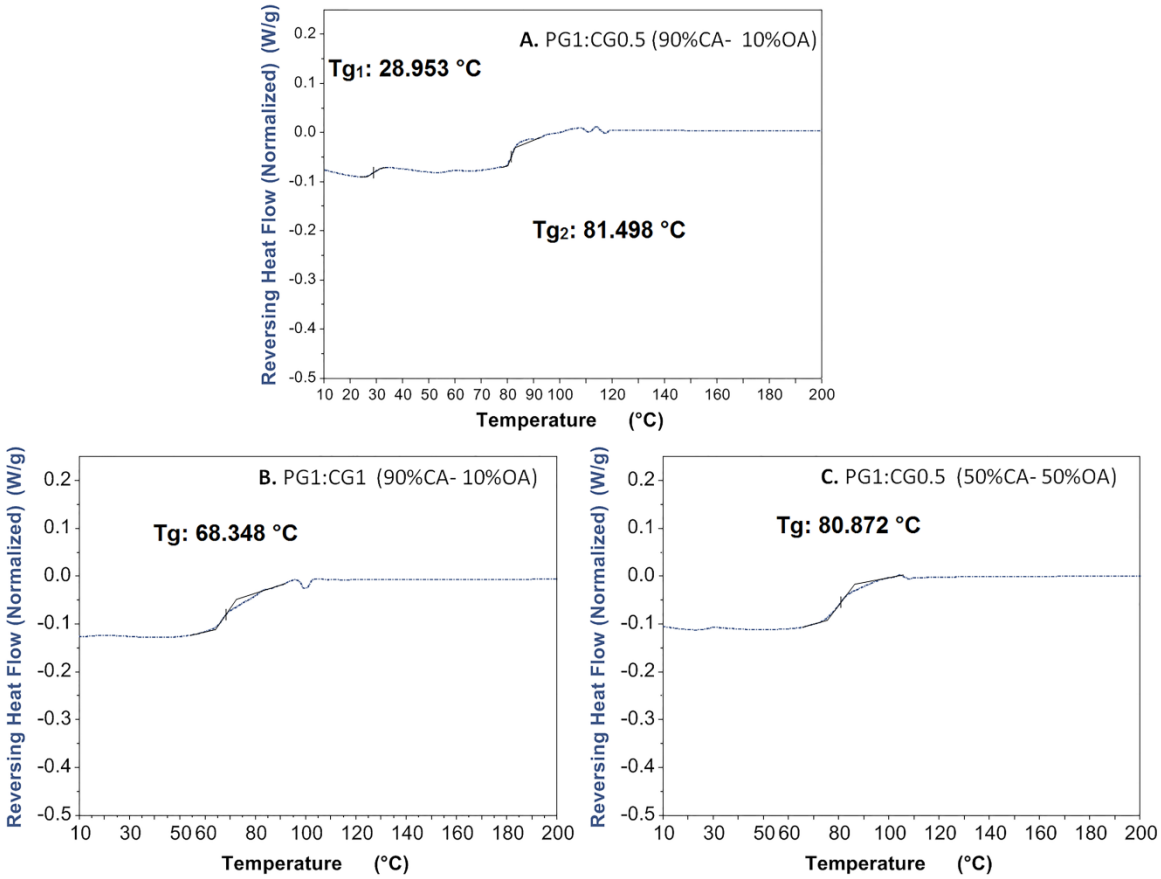

Figure 4.6 Temperature Modulated DSC (TM-DSC) thermograms of A) treatment PG1:CG0.5 (90%CA-10%OA) that exhibits two different glass transition temperatures whereas treatments B) PG1:CG1(90%CA-10%OA) and C) PG1:CG0.5 (50%CA-50%OA) exhibit a single glass transition

4.3.4.2 Degradation behavior measurement

The thermal properties of synthetized hydrogels are directly related to its composition. The TGA and derivative of weight percent curves of PG1:CG0.5

(90%CA-10%OA), PG1:CG0.5 (50%CA-50%OA) and PG1:CG1 (90%CA-10%OA) are shown in Figures 4.7A and 4.7B respectively. The analysis reveals that the treatment PG1:CG0.5 (50%CA-50%OA) exhibits a faster beginning of degradation compared to with regards the other two treatments compared to with regards the other two treatments. This result could be related with the ratio between citric and oleic acid –crosslinking agents- which, for this case is 50%CA-50%OA unlike the other two that exhibit a ratio of 90%CA-10%OA. Furthermore, the treatment PG1:CG0.5 (50%CA-50%OA) has the higher amount of oleic acid. Probably, the deviating behavior may be dependent on the average length of crosslinking chains given by the hydrocarbon structure of oleic acid.

The thermogravimetric analysis shows three stages of hydrogel thermal degradation, see figure 4.7B. First stage goes from 30 to 100°C where there is a loss of weight caused by the loss of bound water. Second stage goes from 100°C to 250°C; in this stage, hydrogels identified as treatments PG1:CG0.5 (90%CA-10%OA) and PG1:CG1 (90%CA-10%OA) loss 20% of their weight, and for treatment PG1:CG0.5 (50%CA-50%OA) 26% of weight loss. Mass loss in this stage could be related to degradation of unreacted glycerol and polymer network pendant groups, as suggested in other studies [35]. This result is consistent with the PG1:CG0.5 (50%CA-50%OA) has a higher weight loss, 26% due to more uncross-linked hydroxyl groups. Last stage goes from 280 to 470°C. In this stage there is a greater weight loss caused by hydrogel backbone degradation. Finally, at temperatures greater than 470°C, treatments PG1:CG0.5 (90%CA-10%OA) and PG1:CG0.5 (50%CA-50%OA) ended up in 14% of ashes, and treatment PG1:CG1 (90%CA-10%OA) in 8% of ashes.

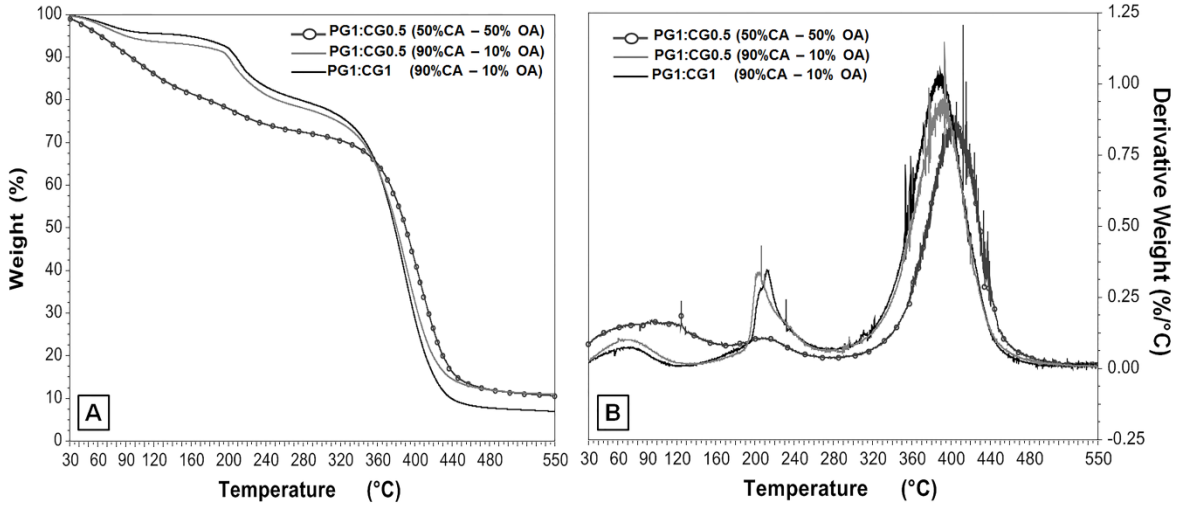

Figure 4.7 TGA (4.7A) and derivative of weight percent (4.7B) of the treatments PG1:CG0.5 (90%CA-10%OA), PG1:CG0.5 (50%CA-50%OA) and PG1:CG1 (90%CA-10%OA).

4.5 Morphological properties

The interior morphology of hydrogel PG1:CG0.5 (90%CA-10%OA) is shown in Fig. 4.8. It was found that the hydrogel exhibits an uneven, rough, heterogeneous and slightly porous structure. The observed hydrogel pore heterogeneity, since exhibit pore diameters from 2 to 62 µm, could be related with the randomness of crosslinking reactions between polyglycerol and citric- oleic acids which have different chain lengths and functional groups. Furthermore, the porous structure has interconnected pores forming open channels for capillary absorption of water, see figure 4.8B.

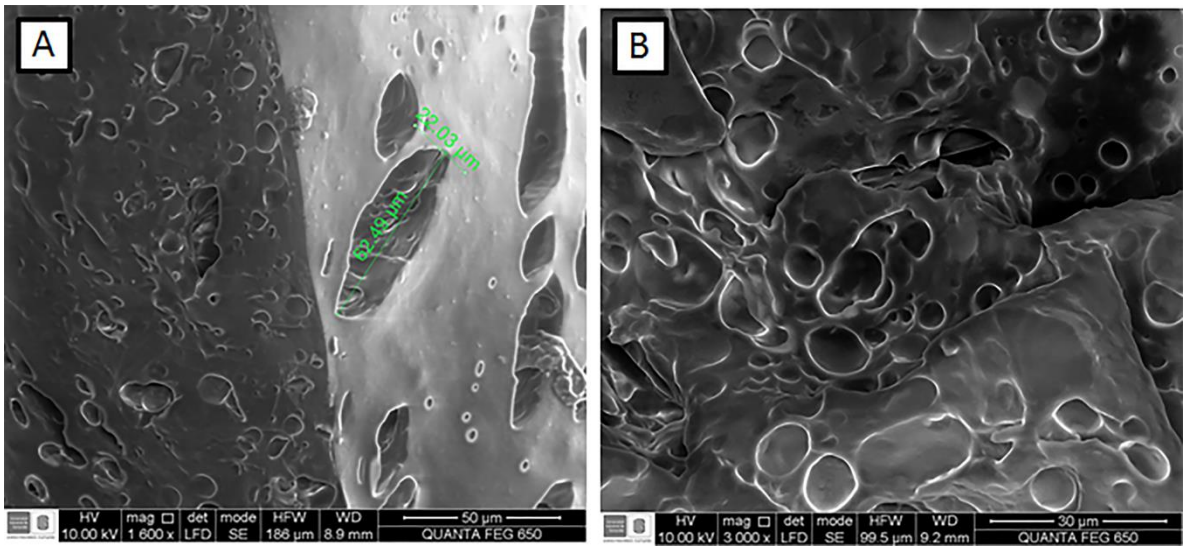

Figure 4.8 SEM micrographs of the hydrogel PG1:CG0.5 (90%CA-10%OA).

4.6 Conclusions

Stimuli – response hydrogels from the crosslinking between glycerol-derived polyglycerol and biodegradable acids –citric and oleic acids- were successfully synthesized. The FTIR analysis showed that the proposed crosslinking reactions were achieved. The swelling behavior and mechanism are related to the cross-linked agent concentration as well as the ratio between citric and oleic acid. The greater swelling behavior at high pH values in addition to slightly acidic values could be associated to the electrostatic repulsion between polymer chains, leading to increasing the free volumes of hydrogel network. The variation of hydrogel swelling capability according with temperatures depends on the glass transition temperatures reported in DSC analysis. TGA analysis showed that degradation behavior of hydrogels is slightly subject to crosslinking agent concentrations. Finally, SEM images exhibited a hydrogel with heterogeneous structure.

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CHAPTER 5

Synthesis and Characterization of Novel Oil-gels Sorbers Based on Polyglycerol

Abstract

Novel oil-gels sorbers derived mainly from biodegradable monomers were successfully synthesized. The differences between functional groups between polyglycerol and polyglycerol-derived oil-gel sorbers were determined by FTIR spectroscopy. The effect of crosslinking degree –given by the variation of DVB concentrations- and the addition of further monomers as palm oil and styrene on oil-gels adsorption capability was determined. Glass transition temperatures of synthesis oil-gels and their degradation behavior were measurement by DSC and TGA analysis, respectively. Morphological study was performed by Scanning Electron Microscopy (SEM). These oil-gels materials are an attractive alternative of other oil sorber polymers since are synthesized mainly from biodegradable monomers.

5.1 Introduction

Oil-gels sorbers are polymeric cross-linked, hydrophobic, three – dimensional networks that are insoluble in non- polar solvents but can absorb large quantities of these molecules [1]. This oil swelling capability makes oil-gels ideal for a variety of applications such as oil spill cleanup, oil/water separation and environmental remediation [2, 3]. The problem being addressed in this study is the synthesis of novel oil-gel based on polyglycerol produced directly from glycerol. The polyglycerol was cross-linked and its hydrophilic-hydrophobic balance was

modified to obtain a final oil-gel material. The Polyglycerol cross-linked agents were oleic acid, palm oil and divinyl benzene.

Several studies have reported the synthesis of oil polymeric sorbers materials. For instance, it was reported an oil-gel crosslinking 1-octene- isodecyl acrylate copolymers with ethylene glycol diacrylate (EGDA) and ethylene glycol dimethacrylate (EGDMA) [4]. In this study was reported that the oil absorbency was influenced mainly by the degree of crosslinking and the hydrophobicity of the copolymer units. Furthermore, bulk and suspension polymerization were used to synthesize octadecyl acrylate/acrylic acid copolymers networks using divinyl benzene as a crosslinker monomer [5]. As a result, oil-gels synthetized by suspension polymerization had better absorption and structural properties than the obtained by bulk polymerization. It has been reported oil gels synthesis based on the polymerization of 4-*tert*-butylstyrene (Tbs), monomer of rigid character and ethylene-propylene-diene (EPDM), monomer of soft oleophilic character both crosslinked with divinyl benzene to obtain high oil absorbency and high gel strength [6]. The aim of this work is to synthetize and characterizes a novel oil gel sorber mainly from biodegradable monomers such as glycerol, oleic acid and palm oil.

Glycerol is a bio-based monomer candidate for sustainable polymeric complexes production, which give to this co-product of the transesterification of vegetable oils a higher added value [7]. The glycerol polymerization product, polyglycerol, can be used as a building block for oil gels sorbers synthesis that may contribute to transform the actual biodiesel industry into a bio-refinery [8]. However, polyglycerols are traditionally synthesized by ring – opening polymerization of glycidol, a toxic monomer [9, 10]. Modifications of hyperbranched polyglycerols, by esterification reactions, have been studied for the preparation of amphiphilic structures. The simple esterification of branched polyglycerols (synthesized from glycerol derivatives) with fatty acids offers potential core-shell amphiphilic structures with applications in biotechnology [11] and removing water-soluble

impurities, in non-polar mediums [12]. Furthermore, as polyglycerol esters can have different behaviors ranging from a hydrophilic character to a completely hydrophobic character depending on the degree of esterification of their hydroxyl groups, they are appropriate structures for the design and synthesis of polymeric cross-linked complexes. To our knowledge there have not been previous reports on oil sorber synthesis from glycerol-derived polyglycerol.

The present study is focus on the development of a novel polymeric material and understanding its structure-properties relation. The novel oil sorber material is synthetized using a glycerol-derived polyglycerol ester of oleic acid, palm oil and styrene as monomers all cross-linked divinyl benzene. A variety of novel polymeric materials have been prepared by the polymerization of natural oils, for instance, palm oil. Their biodegradability opens doors for potential applications in replacing petroleum-based polymers [13]. Natural oils as palm oil as well as the hydrocarbon chains of polyglycerol ester of oleic acid exhibit C=C bonds. This unsaturation allows them the polymerization with aromatic monomers as styrene and divinyl benzene [14, 15]. In this study, palm oil and styrene monomers are used to add soft and rigid segments to oil polymeric sorber with the purpose of tune the mechanical and swelling behavior of polyglycerol-based oil gels cross-linked with divinyl benzene.

A factorial experimental design was performed to study the effect of cross-linked agent concentration, the introduction of soft segments of palm oil, and the addition of rigid chains of polymerizable styrene on final oil gel sorber morphology, absorption capability, and thermal properties. Preliminary test of swelling behavior on light and heavy crude oil solutions –in toluene- were performed. The synthetized oil gel sorbers were characterized using Scanning Electron Microscopy (SEM), Differential Scanning Calorimetric (DSC), Thermogravimetric Analysis (TGA) and Fourier Transform Infrared Spectroscopy (FTIR).

5.2 Experimental

5.2.1 Materials

Glycerol (85%), sulfuric acid (95%), styrene, divinyl benzene and benzoyl peroxide were obtained from Merck. Palm oil and oleic acid used in this study were purchased from the local market. Their compositions are listed in table 5.1.

Table 5.1 Palm oil and Oleic Acid compositions. Characterization was made using a gas chromatography system (Agilent Technologies 6890 series), coupled to a FID detector, using an Agilent DB23 column and SUPELCO 38 FAMES as standards.

Fatty Acid	Palm oil Area Percentage %	Oleic Acid Area Percentage %
Palmitic (C16:0)	9.7037	9.0828
Stearic (C18:0)	3.8958	8.1245
Oleic (C18:1n9c)	27.9593	32.1425
Linoleic (C18:2n6c)	40.7422	36.3093
Linolenic (C18:3n3)	2,4006	3.5647
Eicosenoic (C20:1)	0.5608	4.0572
Others	14.7376	6.719

5.2.2 Experimental procedure

5.2.2.1 Glycerol polymerization and consequent esterification

Glycerol polymerization was carried out in a 50 mL glass reactor equipped with a nitrogen inlet, catalyst feeding, thermometer inlet, and a distillation trap to continuously remove water from the reaction mixture. Temperature was maintained at 160 ℃ using a temperature-controlled heating bath. A vacuum pump was attached to the reactor through the condenser; while, condensation reactions were carried out at pressures below 22 kPa. Sulfuric acid was used as catalyst in an amount of 4.8% w/w. The esterification agent, oleic acid was added –molar ratio Poliglicerol:Oleic acid PG1:OA1, for a complete esterification- to the reaction mass,

just before this reach the gel point, without further addition of catalyst. After the polymerization and esterification process, a washing with distilled water was performed to remove the catalyst.

5.2.2.2 Polyglycerol ester crosslinking

Polyglycerol ester crosslinking was carried out in a 100 mL batch glass reactor. Temperature was maintained at 80 °C using a temperature-controlled heating bath. Polyglycerol ester, styrene, palm oil and divinyl benzene are mixed for 10 minutes –with magnetic stirring- . The initiator concentration was 1% w/w of the total reaction mass. Thus, the benzoyl peroxide –initiator- was added to the reaction mass. Reaction proceeds for 90 minutes. After that, a cure process continues at 100°C for 24 hours in an oven. After the crosslinking process, a washing with toluene was performed to remove the unreacted monomers.

5.2.3 Characterization

Swelling capability in toluene of the cross-linked polymers was performed by ASTM F726-12. The polymer sample was put in a mesh, which had been immersed in toluene. The toluene (or crude oil diluted with toluene 10%) absorbency *(Q)* was calculated according to Eq. 1 [4]. *W* and W_0 are the final and initial weights of oil gel sorbers, respectively. All measurements were done by duplicate.

$$Q = \frac{W}{Wo} \quad \textbf{(1)}$$

A 2^k full factorial experimental design was performed to determine the effect of cross-linked agent concentration, the introduction of soft segments of palm oil, and the addition of polystyrene rigid chains on the swelling behavior of oil gel sorbers. Cross-linked agent concentration –divinyl benzene -, palm oil and styrene were tested at two levels: (i) palm oil: 0 w/w%, and 20 w/w% (ii) cross-linked agent –divinyl benzene-: 5 w/w%, and 10 w/w% (iii) styrene: 0 w/w%, and 10 w/w%, see table 5.2. The total weight of reaction mass is completed with the polyglycerol ester. Samples were randomized and two replicates per level were performed. The

reaction procedure was carried out as described in the experimental procedure section.

Table 5.2 2^k experimental design layout

Parameter	Levels	
Palm Oil [% w/w]	0	20
Divinyl benzene [% w/w]	5	10
Styrene [%w/w]	0	10

Fourier transform infrared Spectroscopy (FTIR) was used to identify functional groups in synthesized oil gel sorbers. The infrared spectra were obtained in transmittance mode in a Thermo Scientific spectrometer (Nicolet 1550 FT-IR). Differential Scanning Calorimetry (DSC) measurements were carried out in a Differential Scanning Calorimeter Discovery, TA Instruments, Inc. (USA), modulated DSC experiment. Modulated amplitude temperature was 1 °C, a period of 60 seconds in a temperature range of -90°C to 300 °C at a heating rate of 3°C/min and nitrogen purge gas (50 mL/min). Thermogravimetric analysis (TGA) was done in a range of temperature from 30 to 500 °C with a heating rate of 5 °C/min using a TGA Discovery from TA Instruments, Inc., equipped with nitrogen purge gas system (50 mL/min). Scanning Electron Microscopy (SEM) images were taken using a Quanta FEG 650 at acceleration voltages of 10 KV.

5.3 Results and discussion

5.3.1 Oil gel sobers synthesis

Oil gel sorbers were synthesized by crosslinking reactions –with divinyl benzene – of the polyglycerol ester, palm oil and styrene monomers, see Figure 5.1. Probably, the reaction involves the formation of the radicals from styrene and divinyl benzene after the decomposition of initiator, benzoyl peroxide. These radicals are then capable of attacking the double carbon bonds of the styrene – allowing growth of polystyrene chains-, divinyl benzene, polyglycerol ester and

palm oil. The involved free radical polymerization reactions allow the formation of three dimensional cross-linked structures that confer stability to oil gel sorbers. The cross-linked network as well as the dangling hydrocarbon chains allows to the sorbers, the affinity with non-polar solvents and the capability to hold them inside the polymer structure sees section 5.3.3.

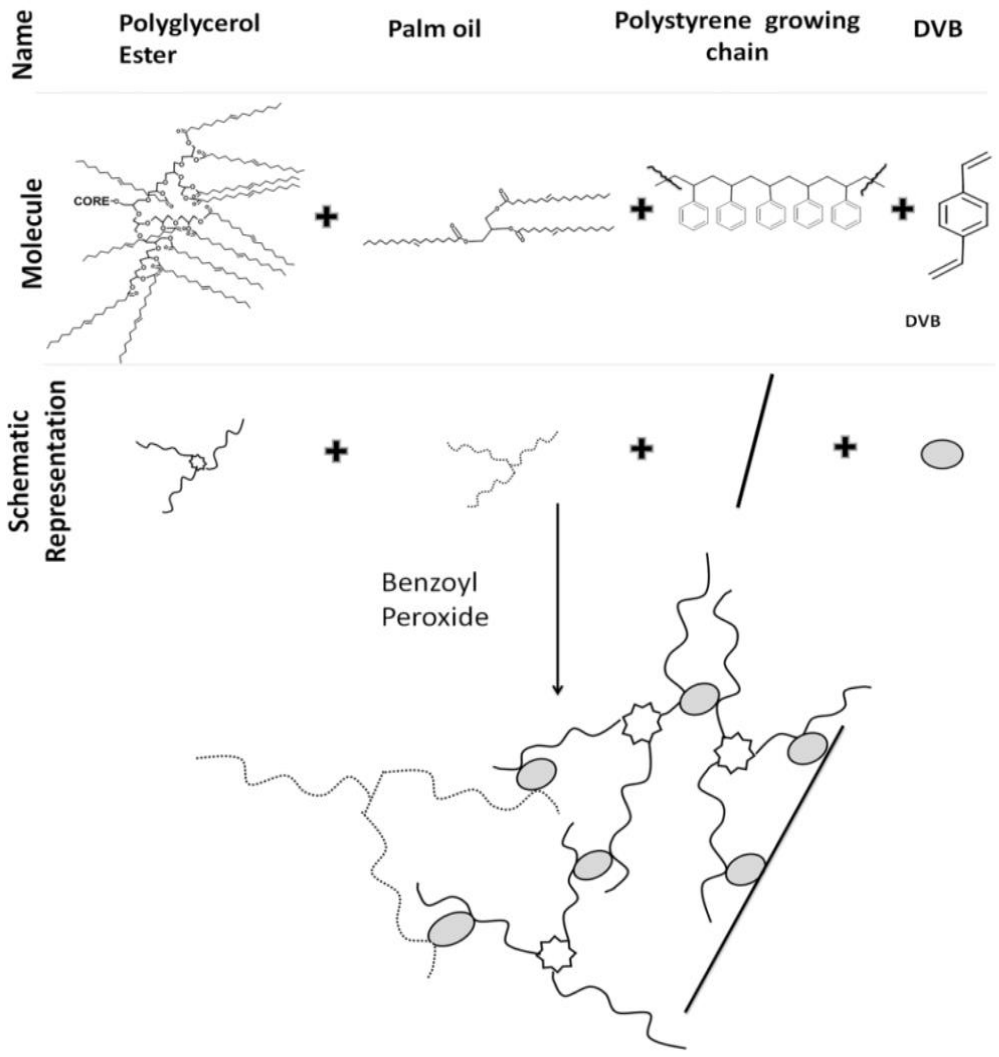

Figure 5.1 Cross-linked network of oil gel sorber. The depicted polymer structure shows just a fragment of the polymer.

5.3.2 FTIR results

FTIR was carried out to characterize the chemical structure differences between polyglycerol and synthesized oil gel, see Fig. 5.2. Polyglycerol spectrum shows hydroxyl group band from 3600 to 3100 cm^{-1} which is indicative of hydrogen bonded alcohol groups [16]. However, in oil gel spectrum the O-H stretch is missing completely. This result is consistent with the consumption of hydroxyl pendant groups of polyglycerol in the esterification reaction with oleic acid to form the hydrophobic derivative. Furthermore, alkyl stretching bands were observed in the two spectra from 3000 to 2800 cm^{-1}. Though, the alkyl band of oil gel presents an intensity increment respect to the same band of polyglycerol as a consequence of the hydrocarbon chains provided by the palm oil and the polyglycerol ester of oleic acid. Absorptions at 1100 – 1000 cm^{-1} are related to stretching of the ether groups that forms the polyglycerol backbone [17]. In addition, absorption at 1730 cm^{-1} in oil gel spectrum is related to the carbonyl *stretch* C=O of aliphatic esters due to the linkage between carboxyl groups of oleic acid and hydroxyl groups of polyglycerol. Finally, the peak at 700 cm^{-1} is related to the deformation of the C-H bond of aromatic rings that confirms the presence of styrene and divinyl benzene.

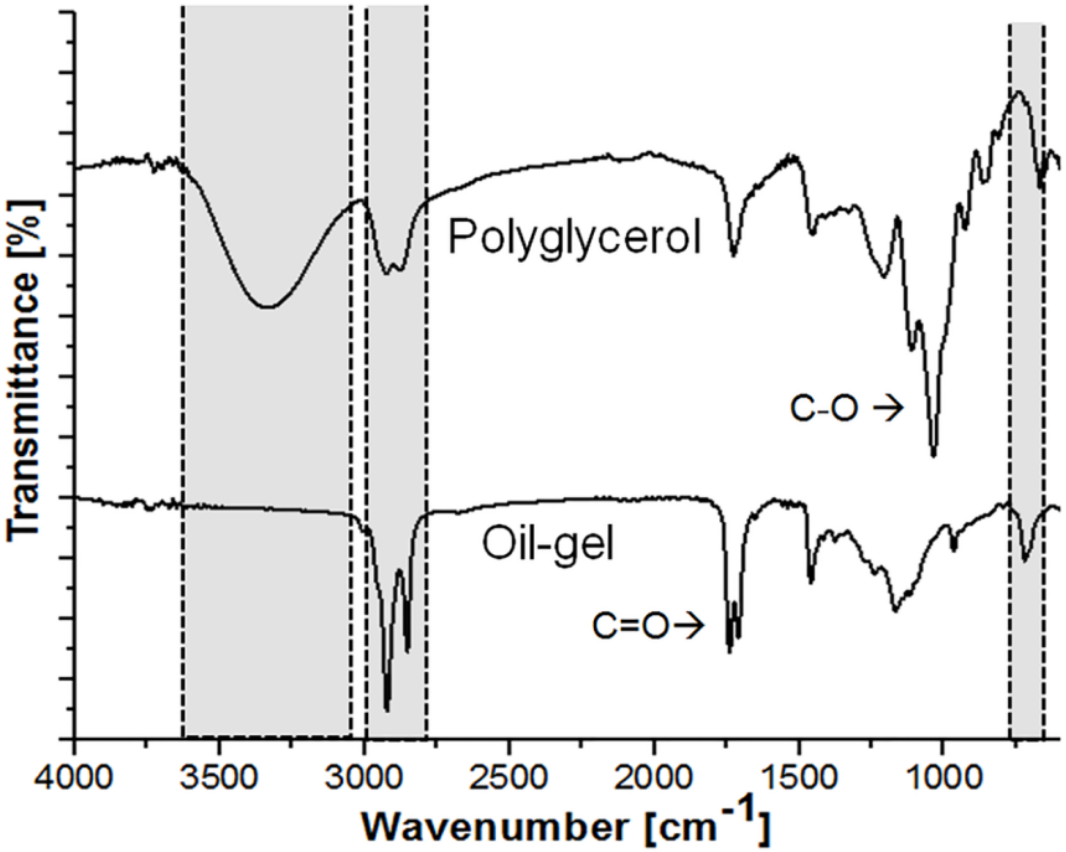

Figure 5.2 FTIR spectra of glycerol – derived polyglycerol and oil-gel sorber derived from polyglycerol. The main peaks associated with the structures are highlighted.

5.3.4 Effect of cross-linked agent concentration, introduction of soft segments of palm oil, and the addition of polystyrene rigid chains on absorption capability

Eight experiments –by duplicate- were established in the experimental factorial design. However, only in six experiments of the initially established, it was possible to obtain materials capable of absorption. It is possible that in the experiment with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 5% (iii) Styrene (St) 0%, the addition of palm oil is more that the needed to form a network with enough cross-linked chains that could allow the oil sorber to hold and not dissolve in toluene. Moreover, in experiment with (i) palm oil (PO) 0% (ii) divinyl benzene (DVB) 10%

(iii) Styrene (St) 0%, the oil-gel sorber is conformed only by the crosslinking between the polyglycerol ester and a 10 %w/w of Divinyl benzene (DVB). It is probable that in this case, the material formed exhibit a high density of crosslinking, which makes it a very brittle material incapable of swelling and very difficult to handle for absorption tests. Furthermore, in both experiments, the styrene content is 0% and consequently the polystyrene chains were not formed. Results of absorption capability of synthesized oil gel sorbers with different concentrations of palm oil, divinyl benzene and styrene are shown in table 5.3.

Table 5.3 Factors levels and response variable of 2^3 factorial design. The factors are Palm oil [%w/w], divinyl benzene [%w/w], and Styrene [%w/w]. Absorption, Q, [g/g], was selected as response variable.

Palm oil [%w/w]	**DVB [%w/w]**	**Styrene [%w/w]**	**Absorption, Q [g/g]**
20	10	10	22.558 ±2.430
20	10	0	0
20	5	10	13.333 ± 0.2057
20	5	0	16.611 ± 0,1184
0	10	10	19.028 ± 2.097
0	10	0	0
0	5	10	10.874 ± 0.7296
0	5	0	16.041 ± 0.1768

The full factorial statistical analysis showed that the interaction between divinyl benzene (DVB) and Styrene (St) (P-value =0.001), the Styrene (St) (P-value = 0.0024) and the Divinyl benzene (DVB) (P-value=0.0186) had a significant effect on absorption capability of oil gel sorbers. The interaction between DVB and St is the factor with the greatest effect on the absorption capability of oil gels sorbers. Furthermore, at fixed values of palm oil of 20% w/w and DVB of 10% w/w whereas St goes from 0% to 10%, the absorption of oil-gel sorber goes from 0 to 22.56 g/g. Thus, if the oil-gel presents the rigid segments of polystyrene, these chains

contribute to free volumes of great size that allow the polymer to hold molecules of toluene. In addition, if the oil gel presents polystyrene chains and not palm oil whereas DVB goes from 5% to 10%, the absorption of oil-gel goes from 10.87 to 19 g/g. This means that if the polymer exhibits polystyrene chains then, the increase of DVB – the crosslinking agent- consequently will increase the cross-linked chains allowing to the oil – gel the absorption of more quantities of toluene.

The absorption behavior of synthesized oil-gels is summarized in figure 5.3. The highest absorption capability – 22.558 $\pm$2.430 g/g- is exhibited by the experiment with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 10% (iii) Styrene (St) 10%. Kulawanda & Douglas [18] reported an oil-gel sorber with a highest toluene absorption capability of 15 g/g in 50 min. Moreover, Farag & El-Seed [1] synthesized an oil-gel sober with maximum toluene absorption capability of 38,8 g/g in 25 hours. In addition Atta & Arndt [4] successfully synthesized polymer cross-linked networks with an absorption capability of more than 60g/g in 50 hours. The synthesized material in this work does not exceed the highest absorption capability of previous studies. However, the oil gel exhibited good swelling behavior with the advantage of being synthesized mainly from renewable monomers.

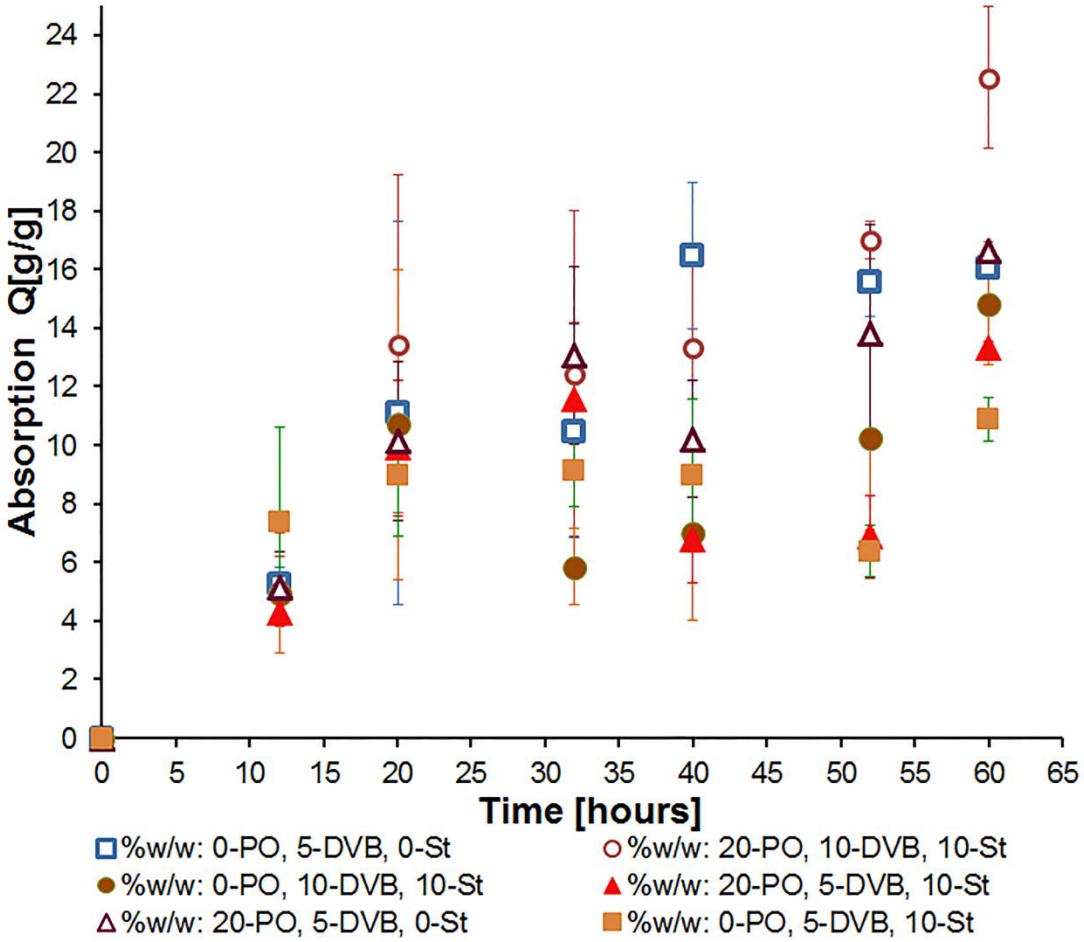

Figure 5.3 Swelling behavior of synthezised oil-gel sobers.

5.3.4.1 Oil-gel absorption capability of crude oil diluted in toluene solutions

The experiment with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 10% (iii) Styrene (St) 10% was tested in crude oil diluted in toluene solutions (10 w/w%). The results are summarized in table 5.4. From this, it can be conclude that the synthesized material is capable of absorbing crude oil solutions. As expected, the absorption capability decrease when the test is made in heavy crude oil in toluene solution. It is probable that the high molecular weight compounds contained in heavy oil difficult the diffusion of the solution through the oil-gel network.

Table 5.4 Oil-gel behavior in the presence of crude oil solutions. API gravity was calculated with API hydrometers ASTM 21H and 24H.

Crude oil solution [10 w/w%]	Light	Heavy
API gravity of crude oil	>21	5.8
Absorption capability [g/g]	2,15	1,57
Time [h]	90	90
Oil-gel appearance after absorption		

5.3.4. Thermal properties

5.3.4.1 Glass transition temperatures measurement

The glass transition temperatures of the experiment with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 10% (iii) Styrene (St) 0%, the experiment with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 10% (iii) Styrene (St) 10% and the experiment with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 5% (iii) Styrene (St) 0% are shown in figure 5.4. It was found that the three above mentioned experiments exhibit more than one glass transition temperature [19]. According to this conclusion, it is suggested that the synthesized oil-gels exhibits immiscible phases, one conformed by the crosslinking between polyglycerol ester and DVB, other

conformed by the crosslinking between palm oil and DVB and finally, a phase conformed by the crosslinking between polystyrene and DVB – if styrene is an initial monomer-.

The three experiments exhibit a first negative glass transition that could be related with the polyglycerol ester cross-linked with DVB phase, since polyglycerol glass transition temperature is in this range (*See section* 2.3.4). Furthermore, in the range between 0 and 65°C, the oil-gels exhibit another glass transition. We hypothesize that could be related with the palm oil cross-linked with DVB phase, since previously had been reported [20, 21] transition temperatures of polymers based on natural oils cross-linked with DVB around these temperatures. However, if the experiment with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 5% (iii) Styrene (St) 0% and the experiment with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 10% (iii) Styrene (St) 0% are compared, the glass transitions probably related with the palm oil cross-linked with DVB phase, are 5°C and 60.5°C respectively. These results suggest that glass transition temperatures are related with the crosslinking degree [22]. If palm oil and styrene content are 20% and 0% respectively, whereas the DVB content goes from 5% to 10%, the mobility of cross-linked chains decreases, which is reflected in an increase of glass transition temperature. In addition, although experiments with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 10% (iii) Styrene (St) 0% and the experiment with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 10% (iii) Styrene (St) 10% exhibit the same DVB content, 10%, it is observed a change from 12.3°C to 60.5°C in their respective glass transition temperatures. This change may depends on the introduction of styrene in the experiment with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 10% (iii) Styrene (St) 10% causing that the DVB being distributed between the different polymer phases and consequently decreases the crosslinking of palm oil phase and its glass transition temperature. As a result of the incorporation of styrene –as a monomer – into the polymer network in experiment with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 10% (iii) Styrene

(St) 10%, is observed a glass transition temperature at 97°C which is related with the polystyrene chains phase in the oil-gel [23].

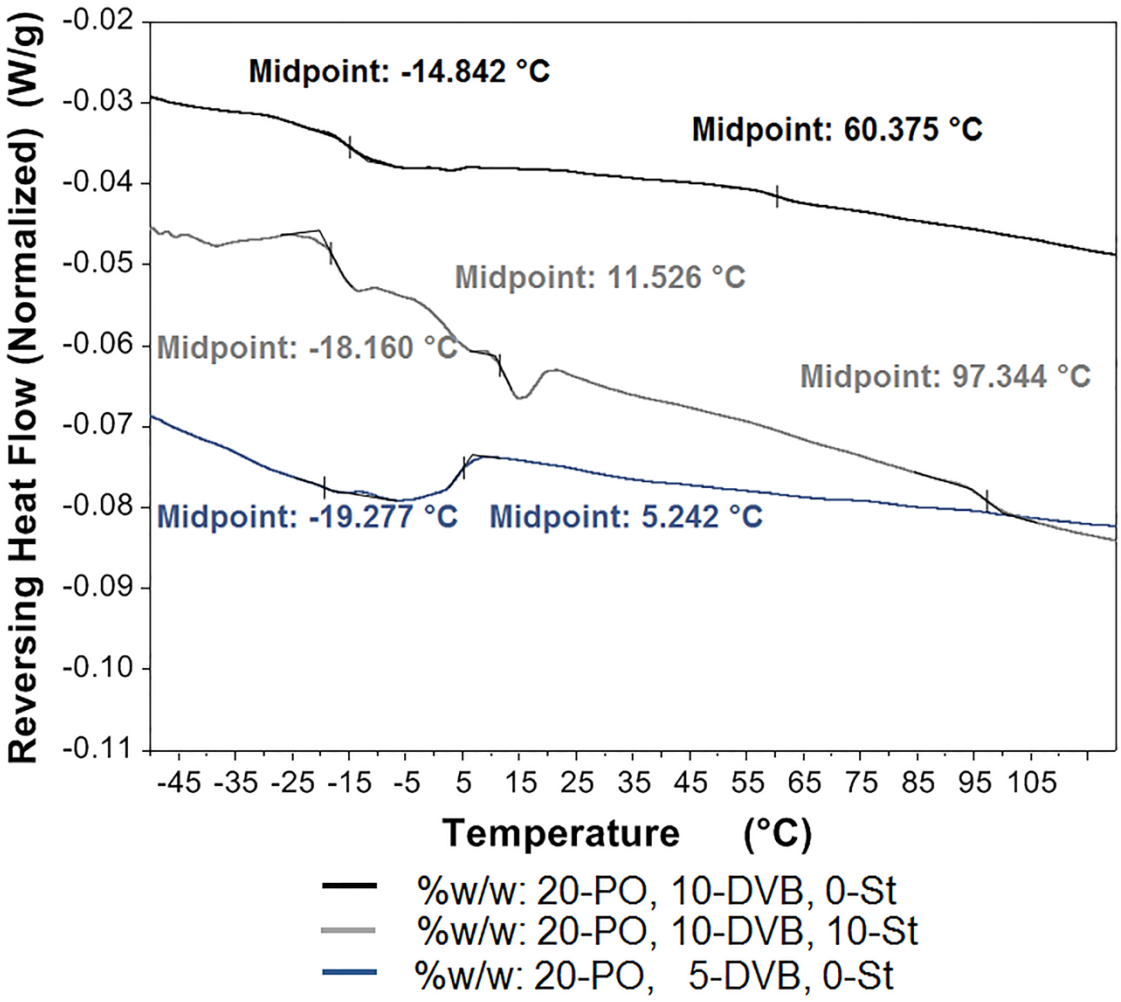

Figure 5.4 Temperature Modulated DSC (TM-DSC) thermograms of experiments with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 10% (iii) Styrene (St) 0%, the experiment with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 10% (iii) Styrene (St) 10% and the experiment with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 5% (iii) Styrene (St) 0%. The three experiments exhibit more than one glass transition temperature.

5.3.4.2 Degradation behavior measurement

The thermal properties of the experiment with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 10% (iii) Styrene (St) 0%, the experiment with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 10% (iii) Styrene (St) 10% and the experiment with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 5% (iii) Styrene (St) 0% are shown in figure 5.5. It was found that the three above mentioned experiments exhibit similar degradation behavior. The thermogravimetric analysis shows two stages of oil-gel thermal degradation, see figure 5.5A. First stage goes from 190°C to 250°C; in this stage, the experiment with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 10% (iii) Styrene (St) 0% % and the experiment with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 5% (iii) Styrene (St) 0%, loss 19.8% and 16.6% of their weight, respectively, whereas the experiment with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 10% (iii) Styrene (St) 10% loss more than the 23% of its weight in the same stage. Mass loss in this stage could be related to degradation of uncross-linked palm oil [24] and uncross-linked polyglycerol ester [25] phases in the bulk polymer. Furthermore, as mentioned above, the experiment with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 10% (iii) Styrene (St) 10% exhibits a higher weight loss in this stage, 23%. This result could be related with the incorporation of styrene monomer into the polymer network. As polystyrene networks are involved in crosslinking reactions with DVB, consequently, the degree of branching of polyglycerol ester and palm oil phases decreases and uncross-linked monomers degraded. Last stage goes from 250°C to 560°C. In this stage there is a greater weight loss caused by the carbonization of the cross-linked polymer network. Finally, at temperatures greater than 560°C, the three experiments ended up in 3% of ashes.

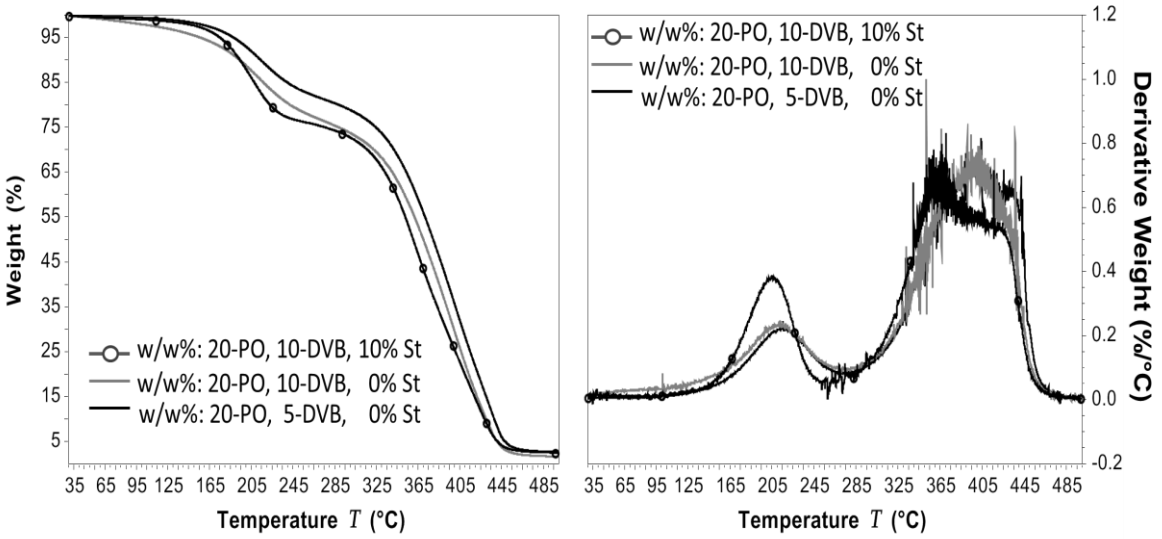

Figure 5.5 TGA (5.5A) and derivative of weight percent (5.5B) of the of experiments with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 10% (iii) Styrene (St) 0%, the experiment with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 10% (iii) Styrene (St) 10% and the experiment with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 5% (iii) Styrene (St) 0%. The three experiments exhibit more than one glass transition temperature.

5.3.5 Morphological properties

The morphology of the experiment with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 10% (iii) Styrene (St) 10% and the experiment with (i) palm oil (PO) 0% (ii) divinyl benzene (DVB) 10% (iii) Styrene (St) 10% are shown in figures 5.6A and 5.6B, respectively. The surface morphology of the oil-gels is irregular, with a rough and porous appearance. If a comparison between two micrographs is made, in figure 5.6A is observed a different phase that could be related with the incorporation of palm oil in the experiment with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 10% (iii) Styrene (St) 10%. Furthermore, figure 5.6B shows a polymer network structure – experiment with (i) palm oil (PO) 0% (ii) divinyl benzene (DVB) 10% (iii) Styrene (St) 10% - with less free volumes than the

exhibited by the other polymer network in figure 5.6A – experiment with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 10% (iii) Styrene (St) 10%-. Both experiments have the same DVB content, 20 w/w%, however the incorporation of palm oil in experiment of figure 5.6A allows lower degree of crosslinking which leads to greater capability of hold the solvent molecules. These results are consistent with absorption test showed in section 5.3.3.

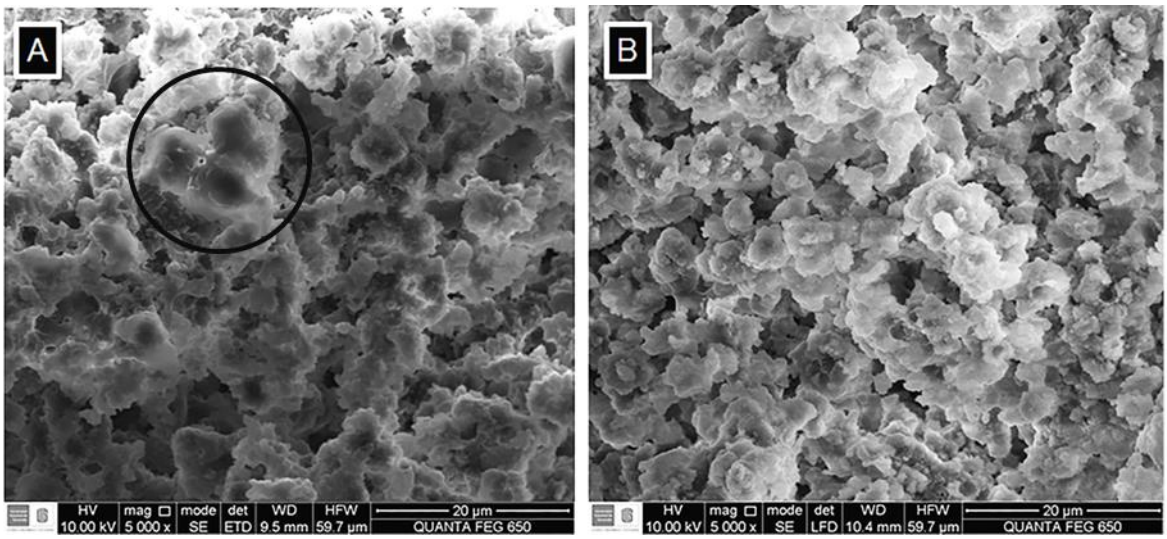

Figure 5.6 SEM micrographs of the experiment with (i) palm oil (PO) 20% (ii) divinyl benzene (DVB) 10% (iii) Styrene (St) 10% -5.6A- and the experiment with (i) palm oil (PO) 0% (ii) divinyl benzene (DVB) 10% (iii) Styrene (St) 10% -5.6B-.

5.4 Conclusions

Novel oil-gels sorbers derived mainly from biodegradable monomers were successfully synthesized. The FTIR analysis showed that the proposed crosslinking reactions were achieved. The absorption capability is related to the crosslinking degree given by the variation of DVB concentration and the addition of additional monomers as palm oil and styrene. The multiple glass transition temperatures reported in DSC analysis suggest that oil-gels are conformed by immiscible phases. TGA analysis showed that degradation behavior of oil-gels is

subject to materials crosslinking degree. Finally, SEM images exhibited oil-gels with morphological differences according with the initial monomers composition that are related with their absorption capability.

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GENERAL CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

Value-added polymer materials from glycerol were successfully synthesized, characterized and their properties evaluated. Polyglycerol, which is the principal product from the polymerization reaction of glycerol, is the backbone of complex polymeric networks that give formation to hydrogels and oil-gels, materials that might have a relevant impact in some fields of industrial applications.

A thorough study of the effect caused by the impurities present in crude glycerol (unrefined glycerol) on the synthesis of polyglycerol, as the main product from the polymerization reaction, revealed that the soap content was the only factor that prevented polyglycerol synthesis as the main product of the polymerization reaction of crude glycerol. The other impurities present in crude glycerol did not prevent polyglycerol synthesis. This finding encourages to investigate and to find a process for soaps removal from crude glycerol, which would lead towards a sustainable production of polyglycerol from unrefined glycerol.

Furthermore, from this study we concluded that the morphology of synthesized polyglycerol is affected by the synthesis conditions and mainly by temperature and sulfuric acid concentration, where sulfuric acid was used as the polymerization catalyst. Specifically, branching degree and hydroxyl number could be varied depending on the synthesis conditions to form polymeric materials with different branching degrees and hydroxyl numbers, which translate in a broader range for further modifications and/or functionalization of the polymeric material. For future work it would be interesting to study the addition of the polyglycerol chain extenders to try to increase the average molecular weight and evaluate the morphology of the final polymer. Being able to synthesize hyperbranched

polyglycerols would broad the range of applications for more complex polymeric materials from glycerol.

A kinetic model describing the polymerization of glycerol to produce polyglycerol was developed. Two important phenomena were found to occur during the polymerization process due to the presence of two resistances acting in parallel. The first one, a chemical resistant, was driven by the chemical reaction and the second one, physical resistance, driven by the mass diffusion process. It was fund that the chemical resistance prevails at lower conversion, while the physical resistance at high conversion where the viscosity of the reaction product increases significantly. A study of the polyglycerol degradation kinetics is recommended for future work.

Novel stimuli – responsive hydrogels were successfully synthesized as a result of the crosslinking reaction between polyglycerol and biodegradable acids –citric and oleic acids. The biodegradable character of synthesized hydrogels increase their potential applications; for instance, as a water reservoir in dry soil. For further work, it is interesting to study the swelling-deswelling kinetics of hydrogels as well as mechanical behavior of material in the field. In addition, it is recommended to study the synthesis of interpenetrating polymer networks (IPNs) between polyglycerol-derived hydrogels and other hydrogel networks such as Poly(N-isopropylacrylamide) (PNIPAAm), which had been previously studied in our research group, to potentiate the stimuli-response properties of the polymer networks.

Finally, novel oil-gel sorbers materials were successfully synthesized as a result of the crosslinking reaction of a polyglycerol hydrophobic derivative and divinylbenzene (DVB). The crosslinking degree and the addition of monomers such as palm oil and styrene, cause a significant effect on toluene absorption capability of polymers, as well as their glass transition temperatures and microstructure. The use of microemulsion polymerization method for the

crosslinking reactions, in order to study the effect of particle size on oil-gel sorbers absorption capacity and thermal properties it is recommended for future studies.

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