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DEP: 2020 DIRECCION DE NUEVAS CREACIONES	EVE: 1 REGISTRO/DEPOSITO/CONCESION/DEPOSITO
TRA: 2 PATENTES DE INVENCION	FOLIOS: 8
ACT: 519 PRESENTACION	

DIRECCIÓN DE NUEVAS CREACIONES

2020
Bogotá, D.C.,

Abogado(a)/Señor(a)
LUZ CLEMENCIA DE PÁEZ

Asunto: Radicación: 14-23102- -3
Trámite: 2
Evento: 1
Actuación: 519
Oficio: 15176
Folios: 8

Patente de Invención	X			Patente de Modelo de Utilidad	
Vía Nacional	X				
Vía PCT (Fase Nacional)		Capítulo I		Capítulo II	
No. Solicitud Internacional					
Fecha de Presentación Internacional					

Como resultado del Examen de Fondo realizado, con fundamento en el Artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se comunica:

1. Documentos estudiados

Descripción:	Rad. N° 14-023102-00000-0000	4/Febrero/2014
Reivindicaciones:	Rad. N° 14-023102-00000-0000	4/Febrero/2014
Dibujos:	Rad. N° 14-023102-00000-0000	4/Febrero/2014

2. Análisis de la Prioridad

Se acepta la reivindicación de Prioridad porque esta solicitud fue presentada dentro del plazo establecido (Art. 9 D 486) y su contenido técnico corresponde con el de la prioridad reivindicada.

3. Objeto de la invención

De acuerdo con lo establecido en el numeral 1.2.2.2 del Capítulo Primero del Título X de la Circular Única para efectos del examen de patentabilidad, se tendrá en cuenta la tasa pagada por el solicitante al momento de comenzar el examen para las reivindicaciones adicionales; esto es que cuando la solicitud contenga más de diez (10)

reivindicaciones y no se haya pagado la tasa complementaria, sólo se estudiarán las cubiertas por la tasa pagada. Por lo tanto se estudiarán las reivindicaciones 1 a 8.

Título de la solicitud: "Proceso de obtención de poliuretanos a partir de aceite de palma y poliuretanos obtenidos" (Ver. Pág. 4 del Rad. N° 14-023102-00000-0000).

El problema técnico planteado en la solicitud consiste en la necesidad de suministrar espumas de poliuretano a partir de materias primas renovables y con características deseables.

Para resolver este problema técnico, la solicitud en estudio proporciona un método de obtención de polioles a partir de aceite de palma, para su posterior polimerización a poliuretano.

El objeto de la presente Solicitud se relaciona con la Clasificación Internacional de Patentes (CIP) C08G 018/036.

4. De la Solicitud de Patente

Reivindicaciones (Art 30 D 486, Art 22 PCT)

Las reivindicaciones 7 y 8 no son claras porque las expresiones "*densidad*", "*módulo de Young*" y "*esfuerzo máximo*" son resultados a alcanzar, lo que no está permitido, no define al producto y/o método porque la invención no queda definida por el resultado a alcanzar, puesto que la reivindicación incluiría no sólo la solución propuesta por el solicitante, sino todas las alternativas presentes o futuras que lleguen a ese resultado. Se sugiere reemplazarla por las características esenciales estructurales que contribuyen a la obtención de ese efecto. En este caso llama la atención que con un mismo procedimiento se obtengan como resultado dos espumas de características diferentes tal como lo reclama la solicitante en las reivindicaciones 7 y 8.

Descripción (Art 28 D 486)

Si bien la descripción de la solicitud presenta métodos en la producción de espumas de poliuretanos a partir de aceite de palma que permiten comparar dichos métodos con el estado de la técnica, los resultados reportados presentan discrepancia con lo solicitado en el capítulo reivindicatorio, ya que para la presente solicitud divisional en la tabla resumen de composiciones y procedimientos se encuentra que (ruta 8) se obtienen polioles intermedios y poliuretanos diferentes a los caracterizados por densidad, módulo de Young y esfuerzo máximo (rutas combinadas 2 y 4), por lo que la presente solicitud carece de sustento para que una persona capacitada en la materia técnica correspondiente pueda ejecutar los métodos reclamados esperando una espuma rígida tal como la reclama la solicitante (Ver ruta 8, experimento 1, Pág. 32, rutas combinadas 2 y 4, experimentos 19 y 25 a 27, Págs. 42, 44 y 45 del rad. N°. 14-023102-00000-0000). Por otra parte en dicha ruta 8 se tiene benceno y dietilenglicol para la producción del polirol, compuestos que no están mencionados en el procedimiento reclamado.

Adicionalmente se solicita indicar la metodología empleada en la determinación del esfuerzo máximo con la que la solicitante diferencia si el producto obtenido es rígido o no ya que para la persona versada en la materia dicha rigidez se puede definir mediante la determinación del esfuerzo de compresión, siendo poco conocido el término esfuerzo máximo como propiedad de rigidez en el campo técnico de las espumas.

5. Determinación del Estado de la Técnica

El estado de la técnica se determinó con base en la fecha de presentación de la solicitud nacional, es decir, el 8 de octubre de 2011.

Consultadas las fuentes de información con que se cuenta, se encontraron los siguientes documentos que anticipan el objeto de esta solicitud.

Ítem	Documento	Título	Fecha de Publicación
D1	Art 1 ¹	"Preparation and characterization of polyurethane foams using a palm oil-based polyol"	14/Agosto/2007
D2	Art 2 ²	"High yield epoxidation of fatty acid methyl esters with performic acid generated <i>in situ</i> "	2008

El documento D1 divulga un método para la obtención de polioles a partir de aceite de palma, terbutanol, glicerol e hidróxido de sodio, y el poliuretano asociado (Pág. 3811. Col. 2, Párr. 2 y Párr. 3, Pág. 3812, Col. 1, Párr. 3 y Párr. 4).

El documento D2 divulga un método para obtener y epoxidar metil ester de ácidos grasos (FAME) (Pág. 467, Col. 2, Párr. 3 a Pág. 468, Col. 1, Párr. 2).

6. Examen de Patentabilidad (Art 14 D486)

Nivel inventivo (Art 18 D486)

La reivindicación 1 consiste en "*Proceso para la obtención de poliuretanos a partir de aceite de palma CARACTERIZADO PORQUE consta de los siguientes pasos*" (Ver Págs. 46 y 47 del Rad. N° 14-023102-00000-0000).

Comparación de las características técnicas **esenciales**, con las del Estado de la Técnica:

Características esenciales	D1	D2
Proceso para la obtención de poliuretanos a partir de aceite de palma caracterizado porque consta de los siguientes pasos	Proceso para la obtención de poliuretanos a partir de aceite de palma (Abstract).	No se menciona
a) Producir metilésteres de ácidos grasos (FAME) a partir de los siguientes pasos:	No se menciona	Se producen metilésteres a partir de aceite de soya (Pág. 467, Col. 2, Párr. 3).
i. Mezclar aceite de palma, metanol e hidróxido de sodio, a una temperatura entre 65°C y 75°C y agitación, durante un periodo entre 1 y 2 horas	No se menciona	Se mezcla aceite de soya, metanol e hidróxido de sodio, a una temperatura de 70°C, durante 1 h y en agitación (Pág. 467, Col. 2, Párr. 3).
ii. Descartar la fase glicerina que se encuentra en el fondo después de la reacción anterior.	No se menciona	Se permite que en reposo se separen dos fases descartándose la fase del fondo rica en glicerina (Pág. 467, Col. 2, Párr. 3).
iii. Lavar la fase de interés obtenida en el primer paso con ácido fosfórico 0,015N a una temperatura entre 55°C y 65°C	No se menciona	Se lava la fase que contiene los FAME con ácido fosfórico 0,015N a una temperatura de 60°C (Pág. 467, Col. 2, Párr. 3).

¹ Tanaka, et al. Bioresource technology. 2008. Vol. 99. Págs. 3810 a 3818.

² Campanella, et al. Chemical engineering journal. 2008. Vol. 144. Págs. 466 a 475.

iv.Descartar los sólidos formados	No se menciona	La decantación es una operación unitaria que permite separar dos fases por lo que si se forman sólidos u otra fase no deseable estos se pueden retirar por decantación (Pág. 467, Col. 2, Párr. 3).
v.Lavar el producto obtenido en el paso anterior con agua a una temperatura entre 55°C y 65°C hasta que el pH esté entre 6 y 8	No se menciona	A 60°C se realizan diversos lavados con agua (Pág. 467, Col. 2, Párr. 3).
vi.Evaporar el producto del paso anterior (FAME) para eliminar el metanol en exceso, a una temperatura entre 75°C y 85°C y durante un periodo entre 2 y 3 horas.	No se menciona	A 60°C y durante 3 horas se remueven por evaporación al vacío las sustancias volátiles para secar los FAME (Pág. 467, Col. 2, Párr. 3).
b)Mezclar los FAME obtenidos en el paso a) con ácido fórmico en presencia de peróxido de hidrógeno	No se menciona	Se mezclan los FAME con ácido fórmico en presencia de peróxido de hidrógeno (Pág. 467, Col. 2, Párr. 5).
c)Lavar el producto obtenido en el paso b) con agua a temperatura entre 50°C y 60°C	No se menciona	Se lava con agua hasta eliminar la acidez (Pág. 468, Col. 1, Párr. 1).
d)Lavar el producto en el paso c) con bicarbonato de sodio al 5%	No se menciona	Se lava con bicarbonato de sodio al 5% y con agua hasta eliminar la acidez (Pág. 468, Col. 1, Párr. 2).
e)Lavar el producto obtenido en el paso d) con cloruro de sodio al 5%	No se menciona	Se lava con cloruro de sodio al 5% (Pág. 468, Col. 1, Párr. 2).
f)Lavar el producto obtenido en el paso e) con agua a una temperatura entre 50°C y 60°C	No se menciona	Se lava con agua hasta eliminar la acidez (Pág. 468, Col. 1, Párr. 2).
g)Evaporar la solución obtenida en el paso c) para eliminar la humedad permitiendo la obtención del polioli	No se menciona	Se remueven por evaporación al vacío las sustancias volátiles para secar el producto epoxidado (Pág. 468, Col. 1, Párr. 2).
h)Tomar el polioli obtenido y mezclarlo con dietilenglicol con agitación	Se tiene que para la producción de poliuretanos se producen epóxidos a partir de aceite de palma y estos epóxidos se tratan con alcoholes polihidricos, siendo un ejemplo el dietilenglicol (Pág. 3811. Col. 1, Párr. 2). Se mezcla el polioli con relaciones desde el 20 al 80% con respecto a la mezcla total que contiene dietilenglicol (Pág. 3812, Col. 1, Párr. 3 y Párr. 4).	No se menciona
i)Adicionar surfactante, DBTL y agua en agitación permanente	Se adiciona un 0,1% de DBTL, un 0,2% de surfactante y un 1% de agua (Pág. 3812, Col. 1, Párr. 3 y Párr. 4).	No se menciona
j)adicionar MDI manteniendo la agitación	Se menciona MDI manteniendo la agitación (Pág. 3812, Col. 1, Párr. 3 y Párr. 4).	No se menciona
k)obtener el poliuretano	Se obtiene un poliuretano semi-rígido (Pág. 3813, Col. 2, Párr. 3).	No se menciona

Los documentos D1 y D2 se consideran el estado de la técnica más cercano a la invención definida en la reivindicación 1, porque divulgan métodos donde se producen poliuretanos a partir de polioles, y polioles a partir de aceites vegetales.

La diferencia entre la invención, definida en la reivindicación 1 y el método del documento D1 consiste en que en D1 no se menciona la obtención de epóxidos a partir de epoxidación de metil ésteres de ácidos grasos.

La diferencia entre la invención, definida en la reivindicación 1 y el método del documento D2 consiste en que D2 no menciona el aceite de palma como materia prima para la obtención del polioliol ni las etapas de síntesis del poliuretano.

No se evidencia algún efecto técnico que logre la diferencia al incluir polioles obtenidos por epoxidación de FAME porque la solución de la presente solicitud genera un producto con las mismas características del poliuretano obtenido en el documento D1.

Por lo tanto, el Problema Técnico Objetivo que pretende resolver esta invención se puede formular así “¿cómo obtener un método para producir un poliuretano a partir de polioles producidos de forma alternativa a la revelada en el documento D1?”.

Sin embargo, la obtención de polioles por epoxidación de FAME, ya está divulgado en el documento D2 que se refiere a un método para obtener y epoxidar metil ésteres de ácidos grasos (FAME) (Pág. 467, Col. 2, Párr. 3 a Pág. 468, Col. 1, Párr. 2).

En consecuencia, una persona normalmente versada en la materia incluiría el método de obtención de epóxidos a partir de FAME de D2 en el procedimiento para la obtención de poliuretano de la anterioridad D1, esperando con certeza lograr el método, como la de la reivindicación 1 de la solicitud, lo cual es considerado obvio y, por lo tanto, sin altura inventiva.

Asimismo, el documento D1 divulga las características de las reivindicaciones dependientes así:

Reivindicación 6: Se obtiene un poliuretano semi-rígido (Pág. 3813, Col. 2, Párr. 3).

Por otra parte la reivindicaciones 2 a 5 son afectadas con el conocimiento del técnico, *“el experto medio deberá poseer experiencia y contar con un saber general en la materia y con una serie de conocimientos en el campo específico de la invención”*³, el cual conoce que:

Reivindicación 2: no se aprecia efecto significativo sobre el método de obtención del polioliol pues las condiciones de temperatura y tiempo de reacción de los FAME con peróxido están enmarcadas dentro de un proceso de optimización lo cual se encuentra dentro de la práctica habitual de la persona versada en la materia que trabaje en la obtención de polioles y su posterior uso en la fabricación de poliuretanos⁴.

Reivindicaciones 3 y 4: el lavado del polioliol obtenido con agua hasta alcanzar un pH de 7⁵.

Reivindicación 5: la evaporación de sustancias volátiles a determinadas temperaturas para purificar el polioliol la cual no modifica la estructura del polioliol⁶.

³Proceso 43-IP-2002, publicado en la G.O.A.C. N° 870, de 9 de diciembre de 2002, caso: formulaciones de péptidos hidrosolubles de liberación retardada.

⁴Purwato E. The synthesis of polyol from rice bran oil (RBO) through epoxidation and hydroxylation reactions. Thesis for master degree. School of chemical engineering. The University of Adelaide. 2010. Pág. 38, Párr. 2 a Pág. 40, Párr.3.

⁵Sinadinovic-Fiser et al. Kinetics of in situ epoxidation of soybean oil in bulk catalyzed by ion exchange resin. Journal of the american oil chemists' society. 2001. Vol. 78 (7). Pág. 726, Col. 2. Párr. 1.

⁶Yang, et al. Thermal analysis of soybean oil based polyols. Journal of Thermal Analysis and Calorimetry. 2009. Vol. 95 (3). (Pág. 980, Fig. 3).

Adicionalmente se reitera que, las reivindicaciones 7 y 8 no mencionan características técnicas y/o características tangibles adicionales que puedan brindarle nivel inventivo al objeto de la reivindicación 1, puesto que se encuentran redactadas en términos de resultados a alcanzar y/o efectos, debido a que la densidad, módulo de Young y esfuerzo máximo dependen del procedimiento y composición empleada para la obtención en este caso del barniz de poliuretano, tal como se aprecia en la tabla resumen de composiciones y procedimientos (ruta 8, experimento 1, Pág. 32, rutas combinadas 2 y 4, experimentos 19 y 25 a 27, Págs. 42, 44 y 45 del rad. N°. 14-023102-00000-0000), en donde se observa adicionalmente que para el procedimiento reclamado en la presente solicitud no se realiza la caracterización de la densidad, módulo de Young y esfuerzo máximo del poliuretano obtenido, caracterización que si se presenta en los poliuretanos obtenidos por otros procedimientos, por lo que es claro que se están obteniendo inicialmente polioles y después poliuretanos diferentes por el procedimiento reclamado en la presente solicitud con respecto a lo solicitado en las reivindicaciones 7 y 8.

7. Conclusión

Los requisitos de Patentabilidad de la presente Solicitud están afectados así:

Item	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	Art 1	1 a 8	Nivel inventivo
D2	Art 2	1 a 8	Nivel inventivo

En referencia al argumento de la solicitante, según el cual el análisis de nivel inventivo se encuentra realizado de forma equivocada al escoger dos documentos y no uno para desarrollar el método problema solución, no se establecieron todas la diferencias entre el documento D1 y la invención y que por lo tanto el problema técnico a solucionar es el de *“¿cómo modificar o adaptar el procedimiento revelado en D1 para obtener FAME a partir de aceite de palma, para luego obtener polioles para luego obtener espumas de poliuretano rígidas?”*, esta Oficina indica que el documento D1 es el antecedente más cercano a la invención y que con dicho documento es que se define el problema técnico a solucionar cuando se compara con la presente solicitud el cual consiste en un problema técnico similar al mencionado por la solicitante y en donde no se presenta un efecto técnico entre los poliuretanos obtenidos a partir de aceite de palma tal como se indica en la metodología de la presente solicitud y el documento D1. Adicionalmente se encuentra que en la ruta 8, experimento 1 se producen espumas pero no se hace su respectiva caracterización que pueda indicar si son rígidas.

Adicionalmente, se coincide con la solicitante en el aspecto que, en este caso, la nueva anterioridad D2 (antes D1) emplea un aceite vegetal diferente al aceite de palma para la obtención del poliuretano y que dichos aceites presentan diferencias en cuanto a las insaturaciones y número de carbonos en los ácidos grasos que componen dichos aceites ni que se obtienen polioles y que por tal motivo no se puede realizar una comparación entre los resultados obtenidos cuando se emplea un aceite de palma u otro en la obtención del poliuretano, pero se reitera que lo que se encuentra por el análisis de nivel inventivo en el documento D2 es la solución al problema técnico, el cual proporciona un método alternativo para la obtención de epóxidos que luego formar polioles, pues la metodología mencionada en D1 proporciona las reacciones necesarias para la obtención del poliuretano de la presente solicitud a partir de epóxidos de aceite de palma. También se encuentra que la ruta 8, experimento 1 es lo más cercano a lo reclamado en la solicitud, pero que allí se tiene a diferencia de la reivindicación 1 dietilenglicol para la producción de polioles, tal como lo establece el documento D1 (Pág. 3811. Col. 1, Párr. 2) y por tal motivo lo que se obtiene por epoxidación tanto en el documento D2 como en la reivindicación 1 son metilésteres epoxidados y no polioles.

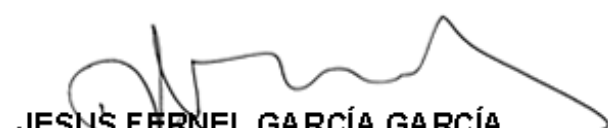
Por otra parte, si bien es cierto que *“un técnico que conozca del arte sabe que cambiar en el proceso de polimerización para la obtención del producto deseado”* según lo indica la solicitante, en el capítulo reivindicatorio se encuentra solo un método por lo que se esperaría obtener espumas con propiedades de módulo de Young, densidad y esfuerzo máximo dentro de un solo intervalo de magnitud y no dos como lo menciona la solicitante, ya que en ningún momento el método reclamado presenta dos diferentes intervalos para cada etapa de proceso, por lo que la persona versada en la materia ve improbable la obtención de espumas con dos propiedades completamente diferentes a partir de un solo método de obtención y más si se tiene en cuenta que las demás solicitudes fraccionarias y la solicitud parental reclaman los mismos productos a partir de métodos completamente diferentes, lo que va en contra de los resultados mostrados en la descripción más específicamente la tabla comparativa de procedimientos realizados y productos obtenidos.

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta (60) días contados a partir del día siguiente de la fecha de notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Se invita al solicitante se sirva indicar, si así lo considera, su renuncia al término faltante de sesenta (60) días para dar respuesta a este requerimiento y presentarla por escrito.

Finalmente, se le recuerda al solicitante que si como respuesta a este requerimiento llegara a modificar el capítulo reivindicatorio y éste contenga más de diez (10) reivindicaciones, no pagará la tasa de modificación voluntaria pero sí la correspondiente al pago por reivindicación adicional.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única No. 10 de 2001.



JESUS FERNEL GARCÍA GARCÍA
Director de Nuevas Creaciones (E)

El anterior requerimiento fue notificado por fijación en lista, de fecha 2014-12-09

Elaboró: Jorge Eduardo Cortazar Gomez
Revisó: Rosa Patricia Tellez Chavarro

Preparation and characterization of polyurethane foams using a palm oil-based polyol

Ryohei Tanaka ^{a,*}, Shigeo Hirose ^b, Hyoe Hatakeyama ^c

^a Department of Biomass Chemistry, Forestry and Forest Products Research Institute, 1, Matsu-no-sato, Tsukuba, Ibaraki 305-8687, Japan

^b Research Institute for Innovation in Sustainable Chemistry, Agency of Industry and Science Technology, Tsukuba, Ibaraki 305-8565, Japan

^c Graduate School of Engineering, Fukui University of Technology, 3-6-1, Gakuen, Fukui 910-8505, Japan

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Abstract

Polyurethane (PU) foams were prepared using a palm oil-based polyol (PO-p). At the first stage, palm oil was converted to monoglycerides as a new type of polyol by glycerolysis. A yield of the product reached 70% at reaction temperature of 90 °C by using an alkali catalyst and a solvent. At the second stage, PU foams were prepared from mixtures of the polyol and polyethylene glycol (PEG) or diethylene glycol (DEG) and an isocyanate compound. Characterization of the foams was carried out by thermal and mechanical analyses. The analyses showed that the chain motion of polyurethane becomes more flexible at the higher PO-p content in the whole polymer, which indicates that the monoglyceride molecules work as soft segments. The study here may lead to a development of a new type of polyurethane foams using palm oil as a raw material.

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Keywords: Palm oil; Glycerolysis; Monoglyceride; Polyurethane foam; Thermal analysis

1. Introduction

Palm oil (PO) is one of the most widely used plant oils in the world. It is produced from oil palm (*Elaeis guineensis*), which is grown in mass plantation in tropical countries such as Malaysia, Indonesia and Nigeria. The oil consists of triglycerides (Tri-G) and diglycerides (Di-G) and McNeill and Berger (1993) reported that 95% of the oil is Tri-G and 5% Di-G and carbons of the carboxyls are ranging 10–20 with or without double bonds. Palm oil is mainly used for food applications, but it is also used in some other industries such as soap, detergent and cosmetic production. In recent years, quite a number of research and development works have been carried out for utilizing palm oil in wide range of application, including bio-diesel fuel (Kalam and Masjuki, 2002; Mohamad and Ali, 2002).

Production of bio-based plastics and composites is thought to be one of the most important issues in the research and development for the protection of global environment (Wang et al., 2002; Yang et al., 2004). Research studies on bio-based polyurethanes have great potential in contributing to such development. In general, polyurethanes have been applied in various products such as thermal insulation and medical implants. The polymer is synthesized by a reaction of an isocyanate compound such as diphenylmethane diisocyanate (MDI) and a polyhydroxyl-containing polymer, i.e., polyol, such as polyethylene glycol (PEG). The preparation of various types of polyurethane products has been extensively studied in recent years, especially containing biomass-originated raw materials (Asano et al., 2001; Hatakeyama, 2002; Hatakeyama et al., 1998; Hatakeyama and Hatakeyama, 2004; Kurimoto et al., 2000; Kurimoto et al., 2001). Moreover, it has become clear from previous studies that the biomass-based PUs have biodegradability (Hatakeyama et al., 1995).

* Corresponding author. Tel.: +81 29 8298270; fax: +81 29 8743720.
E-mail address: ryohei@affrc.go.jp (R. Tanaka).

However, polyols for the polyurethane production are mostly derived from petrochemicals in general. Preparation of the polyurethanes from palm oil may expand the application of the oil in various areas as environment-friendly materials, because of its abundance and renewability. Moreover, it may lead to the replacement of petrochemical products by this naturally occurring plant oil.

There are several research studies of using palm oil for PU preparation (Chian and Gan, 1998; Tuan Noor Maznee et al., 2001). PO consists of mainly triglycerides (Tri-Gs), thus it is necessary to introduce hydroxyl groups to a molecule of Tri-G for urethane reaction. Siwayanan et al. (1999) have reported the preparation of polyols from PO by epoxidation for PU production. By their method, Tri-G molecules were converted to polyols by the reaction with epoxides, followed by the reaction with polyhydric alcohols.

Conversion of triglycerides to monoglycerides is an alternative method for introducing hydroxyls for palm oil, which becomes a 'palm oil-based polyols (PO-p)'. Monoglyceride (Mono-G) is a fatty acid ester of glycerol, and three main processes are widely known for its preparation: (1) glycerolysis of fats and oils with glycerol, (2) enzymatic synthesis by using lipase catalysts and (3) direct esterification of fatty acids or their alkyl esters with glycerol (Noureddini and Medikonduru, 1997). McNeill and Berger have reported a study of the enzymatic synthesis for the preparation of Mono-Gs from palm oil (McNeill and Berger, 1993). However, the glycerolysis has not been applied for palm oil to produce Mono-Gs so far.

In this paper, the first part describes the preparation of Mono-Gs from palm oil as a polyol by glycerolysis. Using this polyol (PO-p), polyurethane foams were prepared and their properties were examined in the second part of this paper.

2. Experimental procedures

The following two distinct processes are described in this section: (1) glycerolysis of palm oil for polyol preparation, and (2) preparation of polyurethane foams using the palm oil-based polyol.

2.1. Glycerolysis of palm oil for polyol preparation

2.1.1. Materials

Palm oil (PO) was kindly provided from MALPOM Industries BHD, Malaysia, as a crude grade (=CPO, crude palm oil). Glycerol, sodium hydroxide (NaOH) and *t*-butyl alcohol (*t*-BuOH) were purchased from Wako Pure Chemical Industries, LTD, Japan. Tetradecane (TD), which was used as an internal standard for the quantification, was also purchased from the Wako. PO and the chemicals were used without further purification.

It has been reported by McNeill and Berger (1993) that the carboxyl groups of palm oil consist of 45.6 wt% of $\text{CH}_3(\text{CH}_2)_{14}\text{COO}-$ (C16:0, palmitic), 36.4 wt%

$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COO}-$ (C18:1, oleic) and 10.3% $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COO}-$ (C18:2, linoleic). Using their precise data for the carboxyls, molecular weights of the PO triglycerides and diglycerides are calculated to be 846.6 and 595.1, respectively, assuming that Tri-G and Di-G have the same carboxyl contents. Moreover, a carboxyl group is expressed as C *x*:*y* in this paper, which *x* is the number of C and *y* the number of double bonds.

2.1.2. Methods

Approximately 20 g of glycerol was placed in a 300 mL three-necked round-bottom flask, equipped with a water-cooling condenser and a thermometer. Accurately weighed PO was added to the flask at the weight ranging 10 ~ 40 g, together with 20 mL of *t*-BuOH as a solvent. Tetradecane (TD) was also accurately weighed to 0.4 g and added to the mixture as an internal standard. 0.2 g of NaOH was then dissolved into the mixture, which works as a catalyst of the glycerolysis.

Placing the flask in a mantle heater, the mixture was heated to approximately 90 °C and was kept for 2 h with continuous stirring. After the reaction completed, the flask was immediately cooled down to the room temperature (*ca.* 20 °C). Ten percent hydrochloride (HCl) (1.8 g) solution was then added to neutralize the alkali catalyst. A homogeneous mixture obtained was dark orange, which was originated from the color of β -carotene naturally contained in PO.

Transesterification of triglyceride (Tri-G) by the glycerolysis undergoes in the presence of an alkali catalyst at an elevated temperature. At this stage, the products must be monoglyceride (Mono-G) and diglyceride (Di-G). Then the Di-G does react with glycerol, resulting in the production of two Mono-Gs. Therefore, one Tri-G can be theoretically converted to 3 Mono-Gs by the glycerolysis.

Quantitative analyses of the Mono-G products were carried out by capillary gas chromatography (GC), according to AOCS (The American Oil Chemists' Society) Official Method Cd 11b-91. A prepared mixture without purification was reacted with bis-trimethylsilyl-trifluoro-acetamide (BSTFA) and trimethylchlorosilane (TMCS) for the conversion of its components to trimethylsilyl (TMS) derivatives. GC analyses of the TMS-derivatized samples were carried out by using a HP6890 GC (Agilent Technologies LTD) equipped with a flame indicator detector (FID) and a capillary column of HP-5 (crosslinked 5% PH ME siloxane).

Prior to the reacted samples, calibration curves were created for two major Mono-G products, i.e., C16:0 and C18:1 Mono-Gs, as C16:0 and C18:1 carboxyls are dominant in the composition of palm oil Tri-Gs. Standard samples of the Mono-Gs were purchased from Sigma Chemical Co. Standard solutions were prepared by dissolving a Mono-G and an internal standard of tetradecane (TD) with various weight ratios in pyridine. The Mono-G in a standard solution was TMS-derivatized as same as the reaction mixture and was analyzed by the GC. Ratios of

the peak area between the Mono-G and TD were calculated and plotted against the weight ratios of the two. Linear relationships were obtained for both C16:0 and C18:1 Mono-Gs, which were used for quantitative analysis of the Mono-Gs in the reacted mixtures.

From the quantitative analysis, the best PO/glycerol ratio was determined for the preparation of a palm oil-based polyol (PO-p), which showed the highest yield of the Mono-Gs. Then the mixture was subjected to the purification process for the removal of *t*-BuOH and unreacted glycerol. At first, the alcohol was removed by the evaporation under vacuum. Then twice a volume of *n*-hexane was added to the remained mixture in a glass container with a screw cap. The container was shaken vigorously to dissolve Mono-G products into the *n*-hexane. After leaving the mixture for overnight, the separation occurred, resulting in an *n*-hexane layer at the top and an unreacted glycerol layer at the bottom. The hexane layer was analyzed by GC and the removal rate of the unreacted glycerol was determined in comparison of the peak areas of glycerol, TD and the Mono-Gs before and after the purification process.

2.2. Preparation of polyurethane foams using the palm oil-based polyol

2.2.1. Materials

A palm oil-based polyol (PO-p) used in this section was prepared by the glycerolysis and the purification process as described in the previous section. Polyethylene glycol (PEG) having molecular weight of 200, diethylene glycol (DEG) and poly (phenylene methane) polyisocyanate (MDI polymer) was commercially obtained.

2.2.2. Methods

A polyurethane (PU) foam was prepared by mixing the PO-p with either PEG or DEG at the beginning. Then 0.1% of dibutyltin dilaurate (DBTDL), a catalyst, was added to the mixture, together with water (1%) and a surfactant (0.2%), forming a 'pre-mixture'. The content of PO-p in each pre-mixture varied between 20 and 80 wt%. Then MDI was added and the reaction was allowed to proceed at room temperature with vigorous stirring. Molecular ratio of isocyanate to hydroxyl groups (NCO/OH ratio) was kept at 1.2 for all samples.

Thermal analyses of thermogravimetry (TG) and differential scanning calorimetry (DSC) were carried out for the PU foams. A Seiko TG/DTA 220-SSC6200 and a Seiko DSC 6200 were used for TG and DSC measurements, respectively. For the TG analysis, an accurately weighed sample (approx. 7 mg) was heated from 25 to 600 °C at the rate of 20 °C/min with N₂ gas purging. The DSC measurement was carried out for a sample (accurately weight, approx. 5 mg) at heating rate of 10 °C/min between –120 and 120 °C under N₂ atmosphere.

Mechanical strengths and moduli of PU foams were determined using a Shimadzu Autograph AG-10TB,

according to JIS K7220. A foam sample was cut in a cube of 1 cm × 1 cm × 1 cm. Compressive strength and modulus of each sample were recorded for three replicates from each PU foam sample. Prior to the measurement, an accurate size and a weight were measured for the sample for calculating its density.

3. Results and discussion

3.1. Preparation of palm oil-based polyol by glycerolysis

Quantitative analysis was carried out for detecting C16:0 and C18:1 carboxyl groups converted to Mono-Gs after the reaction of glycerolysis. As mentioned previously, fatty acids of C16:0 and C18:1 carboxyls account for 45.6 and 36.4 wt%, respectively, making total 82% of the whole fatty acids from PO. When glycerolysis occurs, it seems that carboxyl groups at the C1 and C3 positions of Tri-Gs are more likely to be exchanged by OH groups, compared with the C2 position. It has been reported by Deffense that more than 80% of Tri-G has C16:0 and/or C18:1 at the C1 and/or C3 positions (Deffense, 1985). From this aspect, the quantitative analyses of Mono-G with C16:0 and C18:1 carboxyls were considered to represent the total efficiency of conversion from PO to Mono-G by the glycerolysis.

A mixture obtained by the reaction consists of glycerides (mainly Mono-Gs), unreacted glycerol and PO and *t*-BuOH, together with a trace amount of NaCl and water after the neutralization of the catalyst. GC analysis of the mixture was carried out for determining the reaction products. Assuming that there was no effect on the internal standard of TD during the glycerolysis, the amounts of C16:0 and C18:1 monoglyceride products were calculated by using the calibration curves of the standards and the amount of TD added. Results of three reaction mixtures containing different amounts of PO are given in Table 1.

The production percentage shown in the table is simply calculated by dividing total amount of C16:0 and C18:1 Mono-Gs by an initial amount of PO. Theoretically, one molecule of Tri-G reacts with two molecules of glycerol, i.e., 0.5 of (PO/glycerol) ratio, which results in the production of three Mono-Gs. However, Sample 3 in Table 1 had only reacted approximately 1%, whereas the yield was more than 70% when the glycerol added are far much in excess as Sample 1. These results show that the glycerolysis reaction does occur at reaction conditions applied in this study with the reaction efficiency dependent on the PO/glycerol ratio. On the other hand, nearly 90% of glycerol molecules are left unreacted for producing Mono-Gs at the higher yield. This suggests that an optimum condition of glycerolysis should be examined for the Mono-G production with high efficiency.

By more precise calculation, the conversion rates of the monoglycerides have been determined as molecular masses of fatty acids before and after the glycerolysis, which are

Table 1
Percentage and conversion rate of monoglycerides (Mono-Gs) produced at various PO-glycerol ratios

No.	PO used (g)	PO/glycerol molar ratio	Amount of mono-G produced (g)		Production (%)	Conversion rate (%)	
			C16:0	C18:1		C16:0	C18:1
1	10.2	0.05	3.49	3.89	72.4	60.9	86.5
2	20.0	0.1	1.06	0.945	10.0	9.35	10.7
3	40.0	0.2	0.372	0.122	1.24	1.64	0.690

also given in Table 1. The calculation was carried out as follows:

Conversion rate (%)

$$= \frac{W_{\text{Mono-G}}}{M_{\text{Mono-G}}} \times \left(\frac{W_{\text{PO}}(\text{g}) \times 0.95}{846.6} \times 3 + \frac{W_{\text{PO}}(\text{g}) \times 0.05}{595.1} \times 2 \right) \times \text{mol\% of the carboxyl in PO} \times 100 \quad (1)$$

where $W_{\text{Mono-G}}$ is the monoglyceride produced, $M_{\text{Mono-G}}$ is molecular weight of the Mono-G, W_{PO} palm oil added at the beginning. Moreover, mol% of the carboxyl in PO is 48.4 and 35.1 for C16:0 and for C18:1, respectively.

The result shows a significant difference between C16:0 Mono-G and C18:1 Mono-G, especially at a higher yield. It may arise from the difference in the position of carboxyl groups at triglyceride (Tri-G) molecules. According to Defense, 82–90% of Tri-Gs has C16:0 carboxyl group at the C1 and/or C3 and only 14–17% of them has the carboxyl at the C2 position (Defense, 1985). On the other hand, only 38–41% of Tri-Gs has C18:1 carboxyl group at the C1 and/or C3, but 59–65% at the C2. The analyses carried out in this study have determined only Mono-Gs with a carboxyl group at the C1 (or C3) position. Therefore, the higher yield of 1-Mono-G with C18:1 may be produced efficiently by the reaction between the C2-position C18:1 carboxyl groups and glycerol molecules. On the other hand, the C1-position C16:0 carboxyl groups may be slightly less reactive compared to the C18:1 or, possibly, more 2-Mono-G with C16:0 may be produced. It is necessary to have further studies to investigate the details of the glycerolysis reaction.

A monoglyceride mixture prepared at the same condition as Sample 1 in Table 1 was analyzed by GC before and after the purification. The analysis data clearly shows that the peak of glycerol becomes much smaller after the purification when compared with the peaks of tetradecane (=TD, internal standard) and the Mono-Gs. Extraction of Mono-Gs into *n*-hexane was according to the method by Corma et al. for the separation of fatty products from glycerol (Corma et al., 1998). However, the unreacted glycerol seemed to be partially solubilized in the hexane layer, so that the peak of glycerol was still detected after the purification process. Assuming that there was no loss of TD, C16:0 Mono-G and C18:1 Mono-G, unreacted glycerol in the purified product mixture was analyzed from the comparison of the peak areas between glycerol and these substances. Ratios of the peak areas were calculated from the calibration curves as given in Table 2, which Ratio 1

Table 2
Removal rate of unreacted glycerol from monoglyceride products

	Ratio of peak areas		Removal rate (%)
	Before (ratio 1)	After (ratio 2)	
Glycerol/TD	84.0	8.38	90.0
Glycerol/C16:0 Mono-G	9.66	1.02	89.4
Glycerol/C18:1 1Mono-G	8.29	0.846	89.8

TD: tetradecane; Mono-G: monoglyceride.

Removal rate (%) = (1 – Ratio2/Ratio1) × 100.

expresses the ratio of the peak area of glycerol to that of a standard substance before the purification and Ratio 2 expresses the same peak area ratio after the purification. The removal rate of the glycerol was estimated from the Ratio 1 and 2.

It shows that almost 90% of unreacted glycerol has been removed by the purification procedure. There is no difference among the three standard substances, TD and Mono-Gs, which may indicate that there is no loss in the extraction of Mono-Gs and TD during the purification process. Although the removal of unreacted glycerol was not 100%, the purification of Mono-Gs by using *n*-hexane seemed to be quite effective for the production of Mono-Gs studied here. In addition, a larger scale preparation was carried out to produce the Mono-Gs from 200 g of PO and 400 g of glycerol. The removal rate of unreacted glycerol was 83–85%, calculated from the Mono-G standards. This result may indicate that the purification process employed in this study is applicable to a large scale production of Mono-Gs by palm oil glycerolysis.

3.2. Preparation and characterization of palm oil-based polyurethane foams

Polyurethane (PU) foams prepared in this study were semi-rigid type and the foams became more dark and yellowish with increasing PO-p content in the pre-mixture, probably because of the original orange colour of palm oil. Apparent densities of the PEG-contained foams were scattered between 0.05 and 0.13 g/cm³, whereas the DEG-contained foams had almost the same values of 0.06–0.07 g/cm³. It has been reported that good foam samples have the densities of ca. 0.04–0.05 g/cm³ (Hirose et al., 1994). From this viewpoint, it happened that the DEG-contained foams prepared in this study had better shapes than the foams containing PEG.

Thermal decomposition behaviour of PU foams was studied by thermogravimetry (TG). Fig. 1 shows TG curves of PEG- or DEG-contained PU foams. Each curve expresses the change in the percentage of weight residue, $(m_T/m_{20}) \times 100$, where m_T is the sample weight at temperature T and m_{20} at 20 °C (starting temperature). The curves show a multi-step decrease in this temperature range, especially with high PO-p contents. The starting temperature of the thermal decomposition (T_{di}) was determined as the temperature at which samples show a 1% weight loss. Thermal decomposition temperature (T_d) was determined as the temperature of the cross point of extrapolated baseline and tangent line in a TG curve.

T_{di} , T_d and weight residue at 500 °C were plotted against the PO-p content in the pre-mixture for the PU foams as shown in Fig. 2. For all foams, T_d decreased with increasing PO-p content, whereas T_{di} kept almost constant at ca.

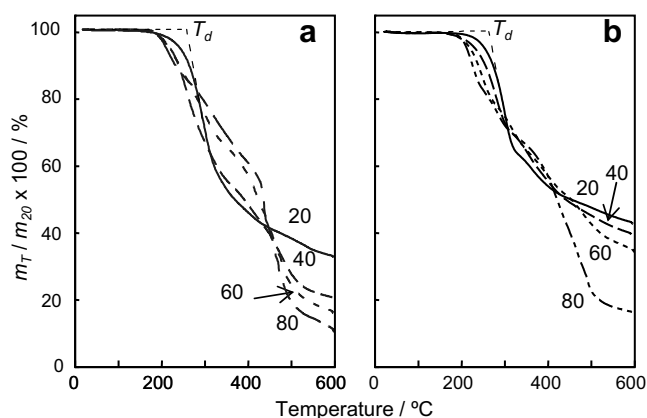


Fig. 1. TG curves of the PEG- or DEG-contained foams having various PO-p contents as indicated on each curve (%): (a) PEG; (b) DEG.

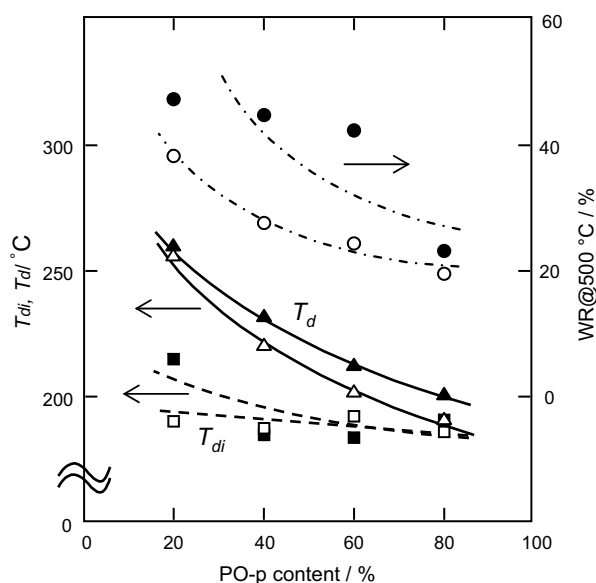


Fig. 2. Starting (T_{di}) and thermal decomposition (T_d) temperatures and weight residues (WR@500 °C) of PU foams having various PO-p content; PEG series: open symbols; DEG series: closed symbols.

200 °C for both PEG and DEG series. From a separate study, thermal degradation of PO-p itself started at very early stage of the TG analysis, i.e., below 100 °C. Kurimoto et al. showed that the degradation of PEG starts at around 200–250 °C (Kurimoto et al., 2001). Moreover, it has been studied that urethane bonds dissociate to form hydroxyl and isocyanate groups at around 250 °C (Hirose et al., 1994). According to these observations, it is considered that the dissociation of urethane bonding starts at T_{di} for all PU foams studied here, irrespective of the PO-p content. The decrease of T_d along the PO-p content, on the other hand, may be due to the introduction of thermally unstable PO-p molecules into PU structure. Therefore, T_d seems to be the decomposition temperature of the polyol molecules, either PO-p or the ethylene glycols.

For weight residue (WR) at 500 °C, the percentage decreased with increasing PO-p content for both PEG and DEG series. As same as the T_d decrease, this indicates that PU structure has become thermally unstable by introducing PO-p segments into ethylene glycol segments of PEG or DEG.

It can also be observed from Fig. 2 that T_d and WR of the DEG series seem to be higher than those of the PEG series, irrespective of PO-p content. Both DEG and PEG have two OH groups in one molecule. Molecular weight of DEG is 106 and that of PEG used in this study is 194, as commercially labelled 200. It means that 100 g of DEG has approximately 2 mols of OH groups, whereas 1 mol for PEG. When the PO-p content is expressed in wt%, total OH content must be higher for a DEG-contained sample than a PEG-contained sample at the same PO-p content. As been mentioned in Section 2.1.2, the molecular ratio of isocyanate groups to hydroxyl groups (NCO/OH) was kept constant at 1.2 for all samples studied here. Therefore, the urethane linkage between OH groups and NCO groups are more in the DEG series and less in the PEG series. Moreover, NCO groups are quite reactive, which may create additional bondings to the urethane linkage. It is also likely to happen in the DEG samples rather than the PEG samples. This may lead to the different behaviour between the both series for the thermal decomposition as shown in Fig. 2.

DSC analysis was carried out to study phase transition of PU foams. Fig. 3 shows stacked DSC curves of PU's containing PEG or DEG. As shown in the figure, two inflectional points were observed by the gap in the baseline due to glass transition (T_{g1} and T_{g2}) for each sample. T_g 's of both series were plotted against the PO-p contents as Fig. 4. The glass transition occurs as a step increase in the heat capacity (C_p) of the sample during heating, which is due to an enhancement of molecular motion in the polymer (Hatakeyama and Quinn, 1994). From each DSC curve, heat capacity difference (ΔC_p) was determined at each transition temperature, ranging 0.02 to 0.07 J/g K for T_{g1} 's and 0.11 to 0.39 for T_{g2} 's. As the ΔC_p at T_{g2} were much larger than the ΔC_p at T_{g1} , it is reasonable to consider that T_{g2} corresponds to relatively large enhancement

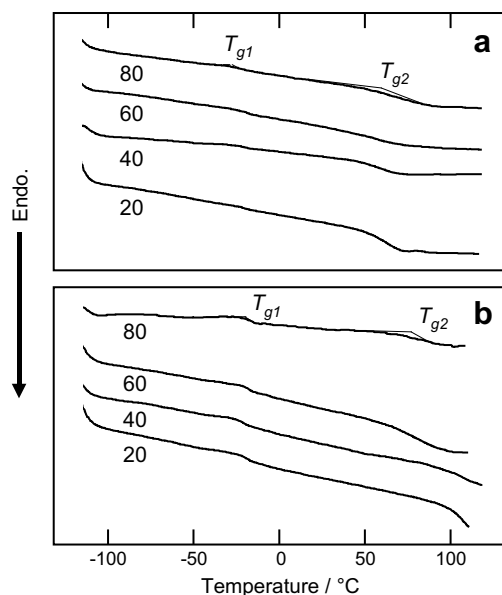


Fig. 3. DSC curves of the PEG- or DEG-containing foams having various PO-p contents as indicated on each curve (%): (a) PEG; (b) DEG.

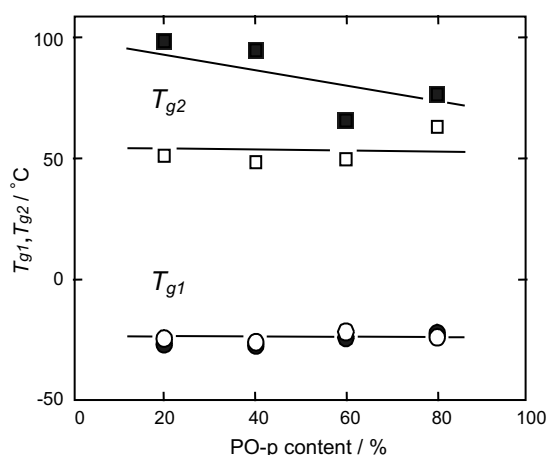


Fig. 4. Relationship between glass transition temperatures (T_{g1} and T_{g2}) and PO-p content; PEG series: open symbols; DEG series: closed symbols.

in molecular motion, whereas T_{g1} is due to rather small movement.

Glass transition at T_{g1} may be attributed to long alkyl carboxyls from the PO-p molecules. The carboxyl groups are assumed to be sticking out from the backbone formed with oxyethylene, glycerol and urethane bonds. Therefore the relaxation of the carboxyls may be independent from the backbone, which leads to constant T_{g1} for all samples.

Enhancement of molecular motion at T_{g2} , on the other hand, may be due to the backbone of PU. As PEG is originally the longer oxyethylene molecule when compared with DEG, the backbone containing PEG is more flexible than that with DEG molecules. This may result in the lower T_{g2} for the PEG series as shown in Fig. 4. However, the dependence of T_{g2} on PO-p content is not clear for both DEG and PEG series. For the DEG series, T_{g2} seems to be decreasing along the PO-p content, whereas it looks almost constant

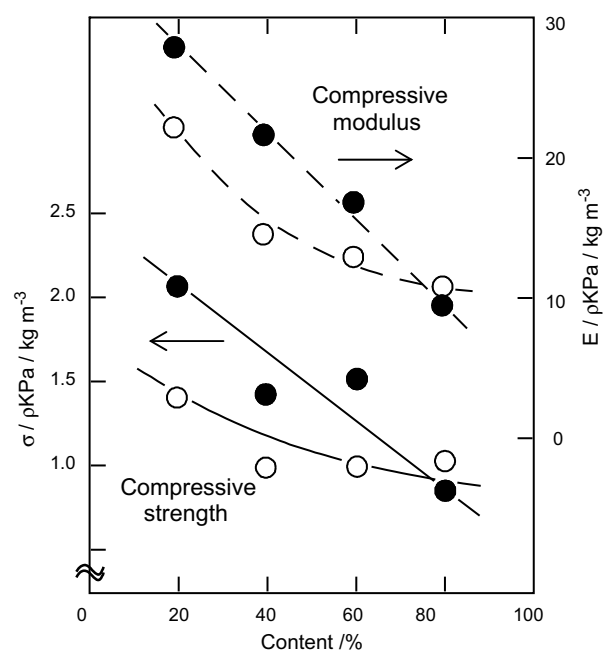


Fig. 5. Changes of compressive strength (σ/ρ) and compressive modulus (E/ρ) along PO-p content; PEG series: open symbols; DEG series: closed symbols.

for the PEG-containing PU. The difference may be related to some complicated alignment and interaction of oxyethylene and PO-p molecules, so that it is necessary to conduct further investigation on the effect of the polyol structure and T_{g2} .

Mechanical properties of the PU foams prepared in this study were also determined as shown in Fig. 5 for compressive strengths (δ) and moduli (E). Each strength or modulus was divided by the sample density (ρ), because these properties are very much dependent on the density and densities of the foam samples were so scattered, especially for the PEG series, as been mentioned previously.

The figure expresses changes of δ/ρ and E/ρ with the PO-p content in the mixtures with DEG or PEG. It is clearly shown that each parameter for both series decreases with increasing the PO-p content. It may be in good agreement with the results of DSC analysis, which suggests that the PO-p molecules work as soft segments in the PU foam. When a pressure is applied, the sample containing more soft segments may be easier to be compressed. Therefore, it reflects in the mechanical properties of the PU foams prepared in this study.

Difference between the DEG series and the PEG series may be the same reason as the phenomena observed at the thermal analyses. The main chain motion in the whole PU is more restricted for the foam containing DEG than that with PEG. So the effect of the PO-p content is the greater for the DEG series.

4. Conclusions

In this study, monoglycerides are derived from palm oil by glycerolysis at the yield of 70%, using an alkali catalyst

and a solvent. After the glycerolysis, 90% of unreacted glycerol is removed by the purification process using *n*-hexane.

Polyurethane foams are prepared using the palm oil-based polyol (PO-p), mixed with polyethlen glycol (PEG) or diethylene glycole (DEG). Chain motion of polyurethane becomes more flexible at the higher PO-p content in the polymer. Monoglyceride molecules, main components of the PO-p, work as soft segments in the whole PU because of the presence of long alkyl chains.

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High yield epoxidation of fatty acid methyl esters with performic acid generated *in situ*

Alejandrina Campanella, Carina Fontanini, Miguel A. Baltanás*

INTEC, Güemes 3450, S3000GLN Santa Fe, Argentina

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ABSTRACT

The impact of the relevant process variables on the reaction of soybean oil fatty acid methyl esters with performic acid (PFA) generated *in situ* using concentrated hydrogen peroxide (up to 60 wt%), to produce an epoxidized product in high yield, is studied in detail. The degree of mixing, temperature, concentration and molar ratios of reactants and/or use of a diluent were considered.

Temperature increases are significantly detrimental for achieving high oxirane numbers, as the selectivity to ring-opening reactions increases. Higher concentrations of either formic acid or H₂O₂ are also harmful (particularly, the carboxylic acid) but much less than temperature.

A proposed alternative process, employing moderate temperature (up to 40 °C) and concentrated H₂O₂, compares favourably with the conventional one; higher conversion combined with high epoxide productivity and selectivity are attainable.

Using economically sound reactants molar ratios, under well-mixed regimes, in which the immiscible polar and organic phases are well dispersed, the epoxidation process can be adequately described using an (equilibrated) two-phase reaction model. The model accounts for both the reversible peracid formation (in the aqueous phase) and the epoxidation reaction proper, together with the attacks on the epoxide ring by formic acid and performic acid (in the organic phase).

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1. Introduction

In recent years, a worldwide interest in renewable resources from the biomass has spurred the manufacture of biodiesel as a more benign fuel, capable of lower environmental impact. Pure or 'neat' biodiesel possesses negligibly low sulphur content, shows an excellent lubricity which extends the lifespan of the engines, is non-toxic and fully biodegradable. It is customarily produced by transesterification of the vegetable oil triglycerides of large-scale crops (e.g., soybean, palm, canola, etc.) with an aliphatic alcohol, usually methanol, employing sodium methoxide (or hydroxide) as homogeneous catalyst. The resulting product is referred to as fatty acid methyl ester (FAME) in the industrial and trade communities.

Thus, FAMES have become widely available commodities which, in view of the stringent requirements of the automobile industry, are produced with great purity. This, in turn, has reopened new avenues to oleochemicals synthesis. One of these alterna-

tives involves transforming the double bonds of the fatty acid molecules into oxirane (epoxide) groups. Epoxides have a high commercial importance and are widely utilized in plastics manufacture, lubricants, detergents and – more recently – as intermediates in chemical reactions [1–5].

Vegetable oils epoxidation can be economically accomplished by reacting the double bonds of FAMES with a peracid (generally peracetic acid), generated for safety reasons *in situ* using hydrogen peroxide. The process usually requires employing an acidic catalyst and, even though traditionally mineral acid have been used due to their lower cost, their utilization prevents the achievement of high yields, because of the opening of the oxirane ring during the course of the main reaction [1,2,6–10].

A possible solution involves using a heterogeneous catalyst, such as ion exchange resins [10,11]. Likewise, amorphous Ti/SiO₂, rhenium or tungsten-based catalysts have been tried, with high yields and/or selectivity [12,13]. Presently, though, all these catalysts are extremely expensive and, so, unsuitable for large-scale commodity manufacturing. An alternative process would use performic acid (PFA) instead of peracetic acid (PAA), as no catalyst is needed to generate the former *in situ* [14–16] and, therefore, the parallel degradation reactions could be –in principle– minimized.

Some kinetic studies concerning the epoxidation of several vegetable oils, and of palm oil FAME as well, with PAA and PFA

* Corresponding author at: INTEC, Instituto de Desarrollo Tecnológico para la Industria Química (Universidad Nacional del Litoral and Consejo Nacional de Investigaciones Científicas y Técnicas), Güemes 3450, S3000GLN Santa Fe, Argentina. Tel.: +54 342 455 9175; fax: +54 342 455 0944.

E-mail address: tderliq@santafe-conicet.gov.ar (M.A. Baltanás).

Nomenclature

IV	iodine value
$[j]^L$	concentration of compound j in the L phase (mol/l)
k	kinetic rate constant (l/(mol s)) or (l ² /(mol ² s))
m_j	distribution constant of compound j
MW	molecular weight
n_j^L	total number of moles of compound j in the L phase (mol)
R	global observable conversion rate (mol/(l s))
S	selectivity
V	total reactor volume (m ³)
V_L	volume of the L phase (m ³)
X	conversion
%Ox	theoretical %Oxirane oxygen

Greek symbol

ϕ	volume fraction
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Subscripts and superscripts

aq	aqueous phase
C=C	unsaturated group
Ep	epoxide group
FA	formic acid
i	FA or PFA
L	generic L phase
org	organic phase
PFA	performic acid
0	initial value

generated *in situ* under homogeneous catalytic conditions, have been carried out in the last years [2,4,5]. These models were pseudohomogeneous (*i.e.*, did not consider the presence of two immiscible phases) but nevertheless they established that the rate-determining step in the epoxidation is always the peracid generation. On the other hand, Rangarajan et al. were able to find the kinetic parameters of the reaction under about the same reaction conditions, but considering a two-phase liquid–liquid reacting system instead [1].

Further work, addressed to obtaining high oxirane values from feedstocks such as soybean or linseed FAMES, in high throughput process units, needs to be done. In this study we have chosen soybean FAME to analyze in detail the epoxidation reaction network when performic acid is used as oxygen carrier and concentrated hydrogen peroxide (up to 60 wt% H₂O₂) is employed. The epoxidation reaction and the parallel, deleterious reactions linked to the oxirane ring opening, are depicted in Figs. 1 and 2, respec-

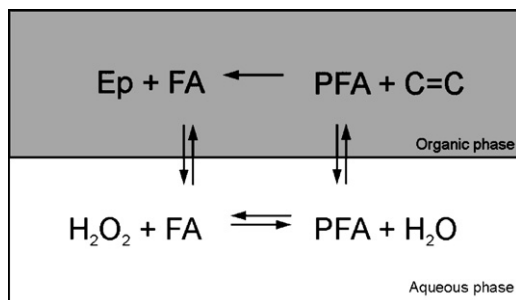


Fig. 1. Double bonds epoxidation reaction in the organic phase, with performic acid (PFA) generated in the aqueous (polar) phase from hydrogen peroxide. The organic acids, PFA and formic acid (FA) 'shuttle' between both liquid phases.

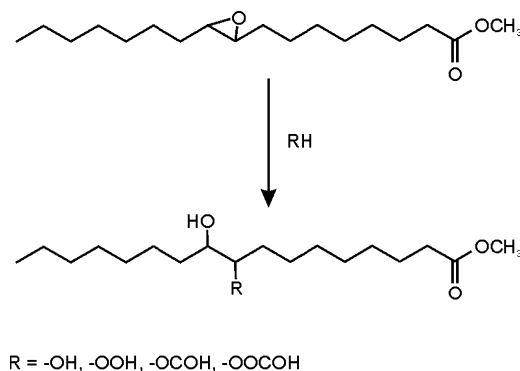


Fig. 2. Main degradation reactions of the oxirane ring.

tively. The influence of several process variables (*viz.*, degree of mixing, temperature, mol ratio of FAME double bonds/hydrogen peroxide/formic acid and solvent addition) on the system was studied, seeking reaction conditions capable of achieving high epoxide yields. In particular, also, the relevant kinetic rate constants pertaining to this heterogeneous liquid–liquid reacting system were found.

2. Experimental

2.1. Materials

Edible, refined soybean oil (Sojola brand, Aceitera General Deheza S.A., Arg.) was used for the production of the FAME stock. Formic acid (99.81%), methanol, benzene and sodium hydroxide were ACS grade and purchased from Fisher Scientific (Pittsburg, PA). Hydrogen peroxide (60 wt%) was supplied by Atanor S.A., a local vendor. Water was doubly distilled (DD) and deionized.

2.2. Preparation of soybean FAME stocks

Batches of the refined soybean oil were interesterified with methanol in a 1000 ml glass reactor furnished with a reflux condenser, at 70 °C. The oil (700 ml) was first heated to the reaction temperature and, next, 270 ml of methanol and 8.28 g of NaOH were added, under moderate stirring. The mixture was so kept for 1 h, after which the agitation was stopped to allow for phase separation (30 min). The heavier, glycerol-rich fraction was discarded and, then, the soybean FAME was washed with 100 ml H₃PO₄ 0.015N at 60 °C. After another three washes with distilled water (100 ml each) at same temperature, the soybean FAME was dried in a rotary evaporator at 10 mmHg and 60 °C, for 3 h.

2.3. Epoxidation of soybean FAME with performic acid generated *in situ*

The reaction was studied in an isothermal, mechanically stirred cylindrical glass reactor (600 ml) provided with a four-blade teflon turbine placed next to the vessel bottom and three teflon baffles on the sides. An internal 316 stainless steel coil allowed refrigerating the reaction mixture and a heating mantle was attached to the temperature controller. A reflux condenser completed the set-up.

About 0.3–0.5 moles of formic acid per mole of double bonds of the FAME were placed into the reactor and heated to the reaction temperature, under agitation. Afterwards, 1.1, 2 or 5 mol of H₂O₂ (~60 or ~30 wt%) were added, drop by drop (1 h in total) and the reaction mixture was held, at constant temperature and under stirring, for several hours (Table 1). Periodically, samples were taken from the reactor; the aqueous phase was eliminated and the organic

Table 1
Reaction conditions and final iodine values (IV_{final}), unsaturation conversion, percent oxirane oxygen ($\%Ox_{\text{final}}$), yield ($\%Y_{\text{final}}$) and selectivity (S_{final}) in the epoxidation of soybean FAME with performic acid generated *in situ* from formic acid and hydrogen peroxide

Run	Molar ratios C=C/H ₂ O ₂ /FA	T (°C)	Stirring (rpm)	[H ₂ O ₂] ^{aq,0} (wt%)	Total duration (min)	IV _{final}	X _{final} ^a	%Ox _{final}	%Y _{final} ^b	S _{final} ^c
Ep-1	1/1.1/0.5	57	1400	59	690	4.7	96.3	3.87	51.8	0.54
Ep-2	1/1.1/0.5	57	350	59	690	7.5	94.2	4.19	56.1	0.59
Ep-3	1/1.1/0.5	40	350	59	690	15.5	87.8	5.71	76.4	0.87
Ep-4	1/1.1/0.5	60	350	35	690	57.2	55.3	3.58	47.9	0.87
Ep-5	1/2.0/0.5	40	350	59	690	4.22	96.7	6.24	83.5	0.86
Ep-6	1/1.1/0.3	40	350	59	690	24.5	80.8	5.55	74.3	0.92
Ep-7	1/5.0/0.3	40	350	59	690	11.1	91.3	5.99	80.2	0.88
Ep-8 ^d	1/0.9/0.5	40	350	59	690	44.2	65.5	4.11	55.0	0.84
Ep-9 ^d	1/1.1/0.5	40	350	59	690	32.1	74.9	4.74	63.4	0.85
Ep-10 ^d	1/1.1/0.3	40	350	59	690	51.1	60.1	3.77	50.5	0.84
Ep-11	1/2.0/0.3	40	350	59	690	19.0	85.1	5.75	77.0	0.90
Ep-12	1/5.0/0.3	40	1000	59	540	5.46	95.7	5.99	80.3	0.84

^a Percent conversion of double bonds calculated as $X = [(IV^0 - IV)/IV^0] \times 100$. The initial iodine value (IV^0) was 129.6.

^b Percent oxirane oxygen yield = $[(\%Ox)/(\%Ox_t)] \times 100$, where $\%Ox_t$ represents the theoretical $\%Ox$ for IV^0 : $\%Ox_t = \{(IV^0/MW_{I_2})/[100 + (IV^0/MW_{I_2})MW_O]\}MW_O \times 100 = 7.4$.

^c Oxirane oxygen selectivity = $[(\%Ox)/(\%Ox_t)] \times [IV^0/(IV^0 - IV)]$.

^d Organic solvent (heptane) added; molar ratio C=C/heptane = 1/2. See text for details.

phase was then thoroughly washed to eliminate acidity and dried, using a rotary evaporator, prior to their derivatization and chemical analysis.

After reaction completion the remaining mixture was washed with a solution of sodium bicarbonate (5 wt%), next with water until complete elimination of acidity in the organic phase and, last, with NaCl (5 wt%). The final product was then dried in a rotary evaporator.

2.4. Oxirane ring-opening studies

For these studies the soybean FAME was epoxidized in depth at low temperature (20–40 °C) with PFA generated *in situ*, using benzene as diluent of the organic phase (C=C/benzene molar ratio = 1/5) to minimize ring opening [2]. To this end, the chosen molar ratio of FAME double bonds/hydrogen peroxide/formic acid was 1/20/2. The soybean FAME, benzene and formic acid were jointly placed into the reactor and then dilute H₂O₂ (30 wt%) was added dropwise, at 20 °C. The reactor temperature was then slowly raised to 40 °C, to complete the reaction (>20 h). The mixture was next washed with distilled water until complete elimination of PFA and FA from the organic phase was achieved, and then with NaCl (5 wt%). Finally, water and benzene were separated from the epoxidized FAME (epFAME) in the rotary evaporator.

The stock of epFAME was used to study the degradation of the oxirane ring by formic acid dissolved in the organic phase and by FA/water and FA/aqueous hydrogen peroxide in the two-phase aqueous/organic mixtures, at 40 °C (Table 2). The epFAME was placed in a three-bore round-bottom flask, furnished with a reflux condenser and a mechanical stirrer. The flask, containing the epFAME, was heated to the desired working temperature in

a thermostated bath. Next, suitable volumes of the reactants, each of them previously thermostated to the reaction temperature, were added to the reactor. Periodically, 5 ml samples were extracted, placed into a separatory funnel, and washed until complete elimination of acidity was achieved, in same manner as in the epoxidation process. The samples were then dried under reduced pressure in the rotary evaporator.

2.5. Distribution constants of formic acid

The distribution constant, or – more appropriately – the equilibrium molar ratio of formic acid in the aqueous (polar) and organic (soybean FAME) phases, was determined at 40 °C.

Thus, different amounts of FA, water and FAME were placed into a round-bottom flask, equipped with a reflux condenser and a mechanical stirrer (see Table 3). The set-up was immersed in a thermostated bath; the mixtures were then stirred (1000 rpm) for 3 h and later left to stand (still at 40 °C) for another 3 h, after which the sample was centrifuged at 10,000 rpm for 10 min. A portion of the aqueous phase was then carefully separated using a syringe and a 0.2-μm teflon filter, to retain any traces of the disperse organic phase.

2.6. Analyses and data processing

The stock of soybean FAME was analyzed to check its water content, by Karl Fisher (Schott TitroLine alpha) and the final concentration of glycerol, mono-, di- and triglycerides by GLC [17], using a Shimadzu GC-17ATF unit and an Agilent column: DB-5HT 15 m, 0.32 mm, and 0.10 μm. Iodine and acid values, as well as fatty acid composition of the FAME were evaluated using AOCS recom-

Table 2
Reaction conditions and percent oxirane oxygen conversion in the study of the degradation of epoxidized soybean FAME (epFAME)

Run	Attacking reactants	Molar ratios	T (°C)	Stirring (rpm)	Total duration (min)	%Ox _{final}	Final oxirane conversion ^a
Deg-1	Formic acid (FA)	epFAME/FA = 1/0.3	40	350	180	5.34	7.11
Deg-2	FA	epFAME/FA = 1/0.5	40	350	180	5.23	7.83
Deg-3	FA, H ₂ O	epFAME/H ₂ O/FA = 1/1.1/0.3	40	350	180	5.27	7.78
Deg-4	FA, H ₂ O	epFAME/H ₂ O/FA = 1/1.1/0.5	40	350	180	5.17	8.97
Deg-5	FA, H ₂ O ₂ ^b	epFAME/H ₂ O ₂ /FA = 1/1.1/0.3	40	350	180	4.96	12.4
Deg-6	FA, H ₂ O ₂ ^b	epFAME/H ₂ O ₂ /FA = 1/2.0/0.3	40	350	180	4.78	17.4
Deg-7	FA, H ₂ O ₂ ^b	epFAME/H ₂ O ₂ /FA = 1/5.0/0.3	40	350	180	4.60	20.5
Deg-8	FA, H ₂ O ₂ ^b	epFAME/H ₂ O ₂ /FA = 1/2.0/0.5	40	350	180	4.30	24.0
Deg-9	FA, H ₂ O ₂ ^b	epFAME/H ₂ O ₂ /FA = 1/2.0/1	40	350	180	3.19	43.7

^a Oxirane oxygen conversion = $[(\%Ox^0 - \%Ox)/\%Ox^0] \times 100$. The initial percent oxirane oxygen ($\%Ox^0$) was 6.7.

^b Aqueous H₂O₂ (59 wt%) was employed. Performic acid was preformed, following Yadav et al. [22] technique. See text for details.

Table 3Distribution constant of formic acid (m_{FA}) between the organic (soybean FAME) and the aqueous (distilled water) phases, at 40 °C

Protocol	Weight (g)			Molar ratios C=C/H ₂ O/FA	[FA] ^{org} (wt%)	[FA] ^{aq} (wt%)	m_{FA}^a ([FA] ^{org} /[FA] ^{aq})	m_{FA}^b
	FAME	H ₂ O	FA					
DC-1	41.22	41.46	4.52	1/10.9/0.5	0.0029	0.097	0.030	0.031
DC-2	50.15	29.02	6.00	1/6.3/0.5	0.0150	0.42	0.036	0.037
DC-3	56.93	19.49	6.99	1/3.7/0.5	0.0076	0.24	0.032	0.031
DC-4	33.59	49.28	2.50	1/15.9/0.3	0.0013	0.047	0.028	0.033
DC-5	57.97	18.79	13.92	1/3.5/1.0	0.015	0.41	0.037	0.038
DC-6	39.88	40.53	7.93	1/11.0/0.8	0.0049	0.16	0.031	0.029
DC-7	40.05	40.52	11.85	1/10.3/1.3	0.0070	0.22	0.032	0.031

^a Experimental.^b Calculated employing UNIFAC ([24] and references therein).**Table 4**

Characterization of the soybean FAME

[H ₂ O] ^a	160 ppm
Monoglycerides ^b	0.85 wt%
Diglycerides ^b	0.11 wt%
Triglycerides ^b	0.13 wt%
Acidity ^c	0.10 wt%
Iodine value ^c	129.59
C16:0 (palmitic) ^c	9.83 wt%
C18:0 (stearic) ^c	3.93 wt%
C18:1 (oleic) ^c	21.0 wt%
C18:2 (linoleic) ^c	57.7 wt%
C18:3 (linolenic) ^c	7.03 wt%
C20:0 (arachidic) ^c	0.32 wt%

^a By Karl Fischer.^b By GLC analysis [17].^c Following AOCS' Official and Recommended Practices [18].

mended practices [18]. The characterization results are shown in Table 4.

The evolution of the epoxidation reaction was followed by measuring the iodine (IV) and percent oxirane oxygen (%Oxirane), also according to AOCS' official and recommended practices [18] using a PE-5 capillary column: 30 m, 0.53 mm, and 1.5 μ m. Only the oxirane value was measured to follow the ring-opening reactions. Each of the reported values of IV or %Oxirane is the mean of three replicates; the coefficients of variation were always less than 9.5%.

The distribution constant of FA was calculated by volumetric titration, using NaOH in the aqueous phase and KOH in the organic phase [18]. The water content in FAME was determined by Karl Fisher.

The kinematic viscosity of the soybean FAME and its epoxide was measured at 40 $\pm$ 0.2 °C, following the ASTM D 445 norm, using a capillary viscosimeter (Cannon-Fenske, Germany) calibrated with the manufacturer's calibration fluids. Likewise, their viscosity (Pa s) was measured with a stress-controlled rheometer Rheostress 80 (Haake Instrument Inc., Paramus, USA). A cone and plate geometry (40 mm diameter, 0.04 rad, 1 mm gap, 1 Hz) was used for all the samples. The experimental results, together with those of some vegetable oils and their epoxides, are shown in Table 5.

3. Results and discussion

3.1. Epoxidation of soybean FAME with performic acid generated in situ

The impacts of the following reaction parameters were considered: the degree of mixing, reaction temperature, mol ratios of hydrogen peroxide and/or formic acid with respect to the double bonds of the FAME and the – eventual – addition of a solvent addition on the system were considered. We focused on those reaction conditions capable of accomplishing both, high unsaturation con-

version and high epoxide yield. In this respect, initial test trials showed that any variation of the French and Minn's recipe [19], namely the slow addition of H₂O₂ to a mixture of the FAME and formic acid was counterproductive and, therefore, the reactants were always added following their suggested procedure. All the experimental conditions are detailed in Table 1. The time course of the iodine value (IV) and the percent oxirane oxygen (%Oxirane) corresponding to each run is shown in Fig. 3.

The analysis of the degree of mixing on the heterogeneous liquid–liquid system (runs Ep-1 and Ep-2, Table 1), where the stirring rates were 1400 and 350 rpm, respectively, for otherwise equal reaction parameters (57 °C and C=C/H₂O₂(59 wt%)/FA=1/1.1/0.5 mol ratios), showed minor differences in the relevant performance criteria under these non-demanding operating conditions: After 690 min the selectivity to oxirane and epoxide yield were somewhat higher in the second case, while the double bond conversion showed a slight improvement under the more vigorous agitation. Nonetheless, the degradation of the oxirane ring was evident in both situations (Fig. 3).

The degree of mechanical agitation, that is, the intensity of turbulence leads to higher interfacial areas between the two immiscible liquid phases and, under mass-transfer controlled regimes, to a faster epoxidation of the double bonds. Higher interfacial areas, in turn, can cause further opening of the oxirane ring, though. Therefore, in view of the previous results and of similar findings as regards this type of coalescing polar/organic mixtures [7–9], and to prevent poor yields as much as possible, the lower mixing regime (350 rpm) was chosen to proceed further (Fig. 3).

The impact of the reaction temperature was scrutinized at a lower level (40 °C), again for C=C/H₂O₂(59 wt%)/FA=1/1.1/0.5 mol ratios (compare runs Ep-2 and Ep-3 in Table 1). Fig. 3 shows that although the reaction was slower at 40 °C, there was no oxirane decomposition with a high selectivity of ~87%. This temperature level was then selected to continue the study.

Table 5

Kinematic viscosity and viscosity of vegetable oils and their epoxides, soybean FAME and epoxidized soybean FAME, at 40 °C

Source	Kinematic viscosity (cSt)	Viscosity ($\times 10^3$ Pa s)
Sunflower oil	28	30
Epoxidized sunflower oil	123	400
High-oleic sunflower oil	41	32
Epoxidized high-oleic sunflower oil	100	110 ^a
Soybean oil	25	32
Epoxidized soybean oil	184	330
Soybean FAME	–	4.7
Epoxidized soybean FAME	–	13

^a At 45 °C.

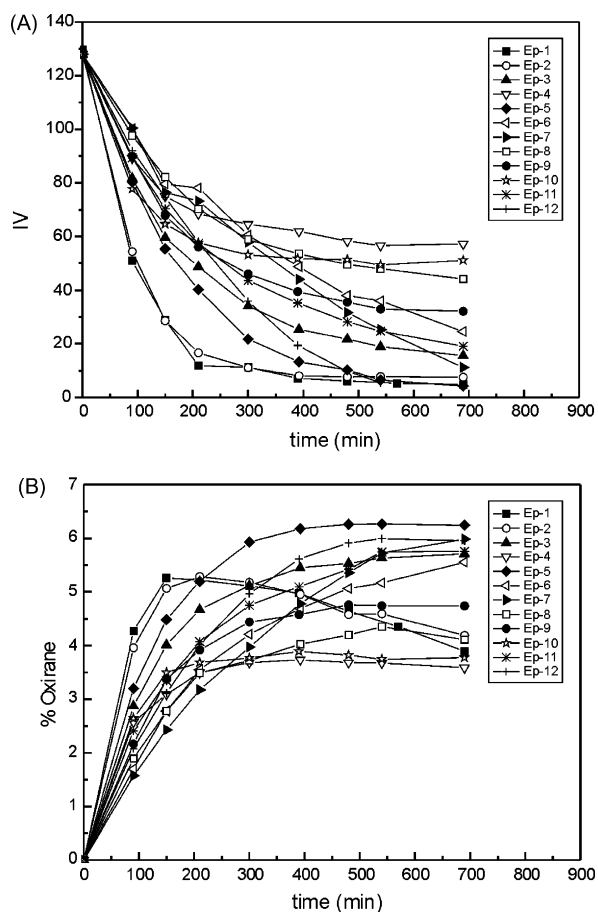


Fig. 3. Iodine value (IV) (A) and percent oxirane oxygen, or oxirane value (%Oxirane) (B), during the epoxidation of soybean FAME with PFA. The different reaction conditions are detailed in Table 1. Lines are meant as a guide to the eye.

The next step was devoted to analyzing the H_2O_2 -to-double bonds molar ratio, by increasing the amount of hydrogen peroxide in the mixture. At the same time, the attack by PAA was moderated by lowering the molarity of formic acid to 0.3 mol per moles of double bonds (runs Ep-6, Ep-11 and Ep-7 in Table 1 and Fig. 3). The final yields after 13 h were 74.3%, 77.0% and 80.2% for $\text{C}=\text{C}/\text{H}_2\text{O}_2$ (59 wt%) ratios equal to 1/1.1, 1/2 and 1/5, respectively. Concurrently, mean-

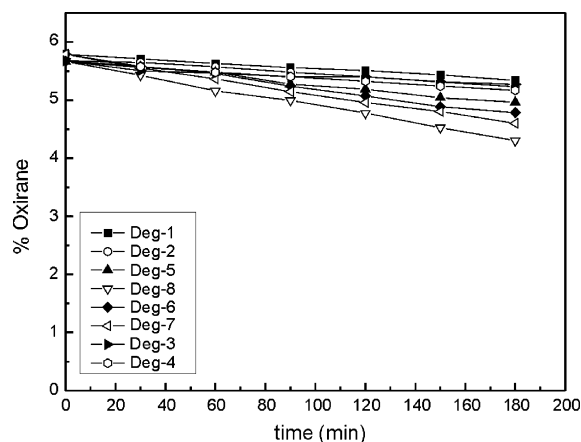


Fig. 4. %Oxirane vs. time during the degradation of epoxidized soybean FAME. The different reaction conditions are detailed in Table 2. Lines are meant as a guide to the eye.

while, the decrease in oxirane selectivity by ring opening – even though the availability of active oxygen had been increased by almost fivefold – was just mild: 0.92 vs. 0.88.

Incidentally, upon using the rather unrealistic (in economic terms) high molarity of hydrogen peroxide, the impact of the degree of mixing in the reacting system was dramatic. This is illustrated in runs Ep-7 and Ep-12, for both of which the mol ratios were set to $\text{C}=\text{C}/\text{H}_2\text{O}_2$ (59 wt%)/FA = 1/5/0.3 but using 1000 instead of 350 rpm in the second case. Then, after only 540 min of reaction time (instead of 690 min) the double bond conversion was significantly higher with about the same oxirane yield, although the final selectivity was somewhat lower already.

The epoxide yield is a strong function of the available amount of FA in the system. Formic acid is indeed crucial for producing enough PFA in the aqueous phase – which then passes to the organic phase to deliver an oxygen atom to the double bonds – but, also, is the main responsible for the opening of the oxirane rings. So, while keeping a moderately high concentration of hydrogen peroxide in the system as well, the concentration of FA was almost doubled (compare runs Ep-5 and Ep-11 in Table 1). Fig. 3 shows that, even though upon using 0.5 mol FA per mol of double bonds the epoxide yield is to some extent lower in run Ep-5, the final %Oxirane after 690 min of reaction is the highest of the set, and the final IV is less than 5 (these low IVs are needed in practical applications), whereas in run Ep-11 the iodine value is still almost 20. Last, it can be appreciated that when the $\text{C}=\text{C}/\text{H}_2\text{O}_2$ (59 wt%)/FA molar ratio was changed from 1/2/0.3 (run Ep-11) to 1/2/0.5 (run Ep-5) the final selectivity did not decay substantially (0.90 and 0.86, respectively).

It is affirmed in the literature that in the absence of an organic diluent it is not possible to achieve optimal oxirane values of epoxidized vegetable oils whenever formic acid is employed at or above 40 °C. Therefore, a non-polar organic solvent was used in the following runs, seeking to maximize the epoxide yield of the soybean FAME. Following US Pat. 3,360,351 [19], in which fatty acid methyl esters are epoxidized with peracetic acid generated *in situ* in presence of heptane, this aliphatic solvent was chosen as well, using a $\text{C}=\text{C}/\text{heptane}$ = 1/2 molar ratio. Yet, comparing runs Ep-6 and Ep-10 (Table 1 and Fig. 3), where the reaction conditions are mild, and otherwise identical: 40 °C, 350 rpm and $\text{C}=\text{C}/\text{H}_2\text{O}_2$ (59 wt%)/FA = 1/1.1/0.3 molar ratios, it is apparent that upon adding the organic solvent the double bond conversion merely improves during the first 3 h, but both the final conversion and epoxide yield after 690 min became severely affected. Owing to dilution effects, lower conversion levels were predictable in the second case but not less selectivity, though (0.92 resp. 0.84) because of the purported moderating impact of organic solvents on the deleterious ring-opening consecutive reactions. These low-performance features can also be appreciated in runs Ep-8 and Ep-9, in which the double bonds to FA ratio was raised to the 'standard' value of 0.5. It is quite likely that aliphatic solvents, rather than aromatic ones (*vide infra*) are less able to protect the epoxide ring from the attack of formic acid, but the subject deserves a more in-depth study.

Perhaps one of the most important findings of the present work is that it shows, as compared with the conventional peracid processes – which employ more dilute hydrogen peroxide (30–35 wt%), at 60 °C – that higher double bond conversion, together with excellent oxirane yield and selectivity can be achieved by using ~60 wt% H_2O_2 and a lower reaction temperature, as exemplified by runs Ep-3 and Ep-4 (Table 1 and Fig. 3), where the conventional $\text{C}=\text{C}/\text{H}_2\text{O}_2$ /FA = 1/1.1/0.5 mol ratios were employed.

Summing up, considering the complete set of conditions explored it is apparent that run Ep-5 gave the best oxirane yield and product quality (lowest IV), in less than 12 h of reaction time (Table 1). Therefore, it is suggested the employment of formic acid for the non-catalyzed epoxidation of FAME with

Table 6Epoxidation of vegetable oils with performic acid generated *in situ* in the presence of benzene (molar ratio C=C/benzene = 1/5) as diluent^a

Oil source	Initial iodine value (IV ⁰)	Total duration (h)	IV _{final}	X _{final} ^b	%Ox _{final}	%Y _{final} ^c	S _{final} ^d
Sunflower oil	120	22	1.78	98.5	6.3	89.4	0.91
High-oleic sunflower oil	83.7	20	0.72	99.1	4.9	98.6	0.99
Soybean oil ^e	132.5	22	1.31	99.0	6.9	89.4	0.90
Soybean FAME ^{f,g}	129.6	>20	4.22	96.7	6.24	83.5	0.86

^a Reaction conditions: double bonds/H₂O₂ (30 wt%)/FA molar ratios = 1/10/0.5; 20–40 °C; 350 rpm; benzene in 30% volume excess with respect to oil source.^b Percent conversion of double bonds calculated as $X = [(IV^0 - IV)/IV^0] \times 100$.^c Percent oxirane oxygen yield = $[(\%Ox)/(\%Ox_t)] \times 100$, where %Ox_t represents the theoretical %Oxirane for IV⁰: $\%Ox_t = \{(IV^0/MW_{I_2})/[100 + (IV^0/MW_{I_2})MW_O]\} \times 100$. The theoretical %Oxirane values for each IV⁰ were 7.03, 5.01 and 7.7 for sunflower oil, high-oleic sunflower oil and soybean oil, respectively.^d Oxirane oxygen selectivity = $[(\%Ox)/(\%Ox_t)] \times [IV^0/(IV^0 - IV)]$.^e Crude soybean oil refined (i.e., degummed, neutralized, bleached and deodorized) in the laboratory was employed.^f Commercial, refined soybean oil (Sojola brand, Aceitera General Deheza S.A., Arg.).^g Run Ep-5 of Table 1. Reaction conditions: double bonds/H₂O₂ (59 wt%)/FA molar ratios = 1/2.0/0.5; 40 °C; 350 rpm.

PFA generated *in situ* at 40 °C, with the following molar ratios: C=C/H₂O₂ (59 wt%)/FA = 1/1.1/0.3 and moderate mixing.

The 'fully epoxidized' soybean FAME was compared with different epoxidized vegetable oils, soybean, sunflower and high-oleic sunflower oil. These fully epoxidized oils were prepared in similar way as the stock of FAME prepared for studying the degradation of the oxirane ring. That is, the oils were epoxidized in depth at low temperature using benzene (C=C/benzene molar ratio = 1/5) as a diluent so as to minimize ring opening. Benzene is a better diluent for epoxidation than heptane (compare Table 6 to runs Ep-8 to Ep-10, Table 1). At similar temperature extremely high oxirane yields and selectivities can be reached, albeit at the expense of large reaction times (they were about equal, ca. 20–22 h, for both the oils and the FAME) and hydrogen peroxide expenditure (as the C=C/H₂O₂ molar ratio was 1/10 in these benzene-moderated experiments).

The viscosity of the set of vegetable oils, soybean FAME and their epoxides was measured at 40 °C (Table 5). It can be promptly appreciated that the viscosity of the epoxidized oils is about an order of magnitude higher than that of the vegetable oils. Likewise, the viscosity of the epoxidized soybean FAME is more than 20-fold higher than that of the methyl ester. These dissimilarities are of course important from an industrial standpoint but, also, because viscosity changes usually bear a profound impact on reaction kinetics and/or reactor design [20,21], as well as on industrial applications themselves.

3.2. Ring-opening studies

Formic acid is soluble in vegetable oils and or their FAME. Therefore, it can degrade the oxirane ring in the organic phase, even at a low temperature. Nevertheless, in the epoxidation process formic acid is mixed with an aqueous solution of H₂O₂, to generate highly reactive performic acid as the oxygen 'shuttler' to the organic phase. This means that *solvated* formic acid is always present in the reacting system.

The experimental data taken under similar working conditions (40 °C; 350 rpm) show that, when solvated formic acid is also available the degradation of the epoxide ring proceeds further. This can be readily appreciated by comparing runs Deg-1 and Deg-2 with runs Deg-3 and Deg-4 (Table 2 and Fig. 4), in which the epFAME/FA molar ratio was 1/0.3 and 1/0.5, respectively. Solvated organic acids are partially dissociated in water (the solvating agent), and this contributes to amplify somewhat the – deleterious – observable reaction rate [9,23].

As for the concentration of formic acid itself, it is also apparent that the higher its molarity is the larger the degradation becomes (compare now the pairs of runs Deg-1 resp. Deg-2, and Deg-3 resp. Deg-4 in Table 2 and Fig. 4).

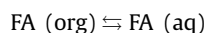
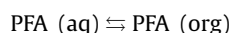
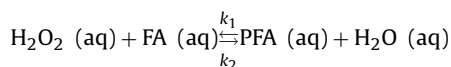
Preformed PFA was used in the set of runs Deg-5 to Deg-9, in which the two-phase liquid–liquid system also contained formic acid and hydrogen peroxide. The peracid was prepared following Yadav et al.'s technique [22] for making peracetic acid: Formic acid was made to react with H₂O₂ (60 wt%) for 24 h, after which equilibrated mixtures of FA, PFA, water and hydrogen peroxide were obtained. These mixtures were then contacted with the epFAME. The different molar ratios employed to perform this set of runs are indicated in Table 2 and, as expected, the degradation of the ring was larger the higher the concentration of either of the PFA precursors, formic acid and H₂O₂, was. However, the impact of the H₂O₂ molarity on ring opening was far less deleterious than that of FA, as shown by comparing runs Deg-5 to Deg-7 versus runs Deg-6, Deg-8 and Deg-9. Therefore the effects of FA were studied in more detail, as it is discussed below.

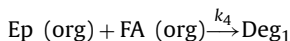
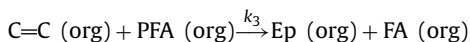
4. Kinetic modelling

4.1. Modelling of the epoxidation reaction (equilibrium two-phase model)

The reacting system features two immiscible phases, one of them polar (the aqueous phase) and the other one organic (Fig. 1). Hydrogen peroxide reacts in the aqueous phase with formic acid (FA) to give PFA, which in turn reacts inside the organic phase combining with the double bonds (C=C) of the unsaturated fatty acid chains to form the epoxide (Ep) ring together with FA. The latter then returns to the aqueous phase to reinitiate the 'oxygen-shuttling' cycle.

As already stated in Section 1, besides the epoxide ring formation several other consecutive, deleterious ring-opening reactions coexist in the system (Fig. 2). To achieve high oxirane value products all of them must be minimized. In recent years, studies aimed at the detailed and systematic evaluation of these reactions have been conducted [7–9]. They indicate that under most of the reaction conditions used in this work, where no homogeneous, aqueous soluble acidic catalyst is used, the only reagents capable of significant ring-opening activity (just in the organic phase) are the carboxylic and percarboxylic acids, FA and PFA. In other words, the following set of reactions suffices to model the reaction system:





So, considering our set-up as a well-stirred, ideal isothermal batch reactor in the slow kinetics regime, where (a) the individual volumes of each liquid phase remain nearly constant and (b) the concentration gradients in both liquid phases are negligible, so the bulk concentrations are related by the partition equilibria of FA and PFA, the following *overall* mass balances for each component in the equilibrium two-phase model can be written:

Mass balances for H_2O and H_2O_2

$$\frac{dn_{\text{H}_2\text{O}_2}^{\text{aq}}}{dt} = \frac{V_{\text{aq}} d[\text{H}_2\text{O}_2]^{\text{aq}}}{dt} = (-R_1^{\text{aq}} + R_2^{\text{aq}}) V_{\text{aq}} \quad (1)$$

$$\frac{d[\text{H}_2\text{O}_2]^{\text{ad}}}{dt} = (-R_1^{\text{aq}} + R_2^{\text{aq}}) \quad (2)$$

$$\frac{dn_{\text{H}_2\text{O}}^{\text{aq}}}{dt} = -\frac{dn_{\text{H}_2\text{O}_2}^{\text{aq}}}{dt} \quad (3)$$

where

$$R_1^{\text{aq}} = k_1^{\text{aq}} [\text{FA}]^{\text{aq}} [\text{H}_2\text{O}_2]^{\text{aq}} \quad (4)$$

$$R_2^{\text{aq}} = k_2^{\text{aq}} [\text{PFA}]^{\text{aq}} [\text{H}_2\text{O}]^{\text{aq}} \quad (5)$$

Mass balance for formic acid

$$n_{\text{FA}} = n_{\text{FA}}^{\text{aq}} + n_{\text{FA}}^{\text{org}} = [\text{FA}]^{\text{aq}} V_{\text{aq}} + [\text{FA}]^{\text{org}} V_{\text{org}} \quad (6)$$

Considering the volume fractions of the aqueous and organic phases, ϕ_{aq} and ϕ_{org} together with the partition equilibrium of FA,

$$m_{\text{FA}} = \frac{[\text{FA}]^{\text{org}}}{[\text{FA}]^{\text{aq}}} \quad (7)$$

Eq. (6) can be recast, upon derivation, as follows:

$$\frac{dn_{\text{FA}}}{dt} = \left(\frac{1 - \phi_{\text{org}}(1 - m_{\text{FA}})}{m_{\text{FA}}} \right) V \frac{d[\text{FA}]^{\text{org}}}{dt} \quad (8)$$

Besides:

$$\frac{dn_{\text{FA}}}{dt} = \frac{dn_{\text{FA}}^{\text{aq}}}{dt} + \frac{dn_{\text{FA}}^{\text{org}}}{dt} = (-R_1^{\text{aq}} + R_2^{\text{aq}}) V_{\text{aq}} + R_4^{\text{org}} V_{\text{org}} \quad (9)$$

Equating Eqs. (8) and (9) and rearranging:

$$\frac{d[\text{FA}]^{\text{org}}}{dt} = \left(\frac{1 - \phi_{\text{org}}(1 - m_{\text{FA}})}{m_{\text{FA}}} \right)^{-1} [(-R_1^{\text{aq}} + R_2^{\text{aq}}) \phi_{\text{aq}} - R_4^{\text{org}} \phi_{\text{org}}] \quad (10)$$

where as it is fully explained in what follows:

$$R_4^{\text{org}} = k_4^{\text{org}} ([\text{FA}]^{\text{org}})^2 ([\text{Ep}]^{\text{org}}) \quad (11)$$

Mass balance for performic acid

Proceeding in similar fashion as above, the following expression results:

$$\frac{d[\text{PFA}]^{\text{org}}}{dt} = \left(\frac{1 - \phi_{\text{org}}(1 - m_{\text{PFA}})}{m_{\text{PFA}}} \right)^{-1} [(R_1^{\text{aq}} - R_2^{\text{aq}}) \phi_{\text{aq}} - R_5^{\text{org}} \phi_{\text{org}}] \quad (12)$$

where

$$m_{\text{PFA}} = \frac{[\text{PFA}]^{\text{org}}}{[\text{PFA}]^{\text{aq}}} \quad (13)$$

and

$$R_5^{\text{org}} = k_5^{\text{org}} ([\text{PFA}]^{\text{org}})^2 ([\text{Ep}]^{\text{org}}) \quad (14)$$

Mass balance for FAME unsaturation (double bonds: $\text{C}=\text{C}$)

$$\frac{dn_{\text{C}=\text{C}}^{\text{org}}}{dt} = \frac{V_{\text{org}} d[\text{C}=\text{C}]^{\text{org}}}{dt} = -R_3^{\text{org}} V_{\text{org}} \quad (15)$$

$$\frac{d[\text{C}=\text{C}]^{\text{org}}}{dt} = -R_3^{\text{org}} \quad (16)$$

where

$$R_3^{\text{org}} = k_3^{\text{org}} [\text{PFA}]^{\text{org}} [\text{C}=\text{C}]^{\text{org}} \quad (17)$$

Mass balance for the epoxide groups (Ep)

$$\frac{dn_{\text{Ep}}^{\text{org}}}{dt} = \frac{V_{\text{org}} d[\text{Ep}]^{\text{org}}}{dt} = (R_3^{\text{org}} - R_4^{\text{org}} - R_5^{\text{org}}) V_{\text{org}} \quad (18)$$

$$\frac{d[\text{Ep}]^{\text{org}}}{dt} = (R_3^{\text{org}} - R_4^{\text{org}} - R_5^{\text{org}}) \quad (19)$$

The distribution constants of formic acid for each reaction condition were experimentally determined (Table 3). The order of magnitude of these values is quite similar to those of acetic acid [1,24]. Table 3 also contains the m_{FA} values predicted using UNIFAC (UNIQuac Functional-group Activity Coefficient) ([24] and references therein), which are very similar to the measured ones. Therefore, the distribution constant of performic acid was estimated employing UNIFAC.

The kinetic rate constant of the epoxidation reaction, k_3^{org} , was calculated employing Eqs. (1)–(19), using averages of the experimental values of m_{FA} (0.035) and the predicted values of m_{PFA} (0.095). The kinetic rate constants for the formation of PFA in the aqueous phase are well known, given the similar molecular structure of acetic and formic acids [1]. At 40 °C these values are the following: $k_1^{\text{aq}} = 5.5 \times 10^{-4} \text{ l}/(\text{mol min})$ and $k_2^{\text{aq}} = 7.5 \times 10^{-4} \text{ l}/(\text{mol min})$. The remaining kinetic rate constants corresponding to the attack of FA and PFA on the epoxide ring in the organic phase, k_4^{org} and k_5^{org} , were calculated as described below.

4.2. Modelling of the degradation reaction caused by FA and PFA

Fully epoxidized soybean FAME (epFAME) was used to study the degradation of the oxirane ring by formic and performic acids at the chosen reaction temperature (40 °C). To this end, the ring opening by pure FA (i.e., only in the organic phase) as well by an aqueous solution of the carboxylic acid were studied, together with designed runs where both FA and PFA were present (Table 2).

The general constitutive equations expressing the attack by neat carboxylic or percarboxylic acids on the epoxide ring in the organic phase can be written as

$$R_i^{\text{org}} = k_i^{\text{org}} ([I]^{\text{org}})^{\alpha_i} ([\text{Ep}]^{\text{org}})^{\beta_i} \quad (20)$$

where $i = \text{FA}$ or PFA , whereas, for aqueous-solvated acids, k_i^{org} is equal to $k_{\text{in}} + k_{\text{IR}} [\text{H}^+]$ and, in turn, $[\text{H}^+] = f_i ([\text{FA}]^{\text{org},0})$. In general, though, $k_{\text{in}} \ll k_{\text{IR}} [\text{H}^+]$ [21].

In previous work, and in agreement with other research groups [1,6], we reported that each of the oxirane ring-opening reactions is first order with respect to the molar concentration of the epoxide groups in the organic phase [7–9]. We found, also, that the attack by acetic and peracetic acids was second order with respect to their concentration. Thence, considering the close structural similarity

Table 7

Kinetic rate constants corresponding to the degradation (opening) of the epoxide ring of soybean FAME in the organic phase caused by FA and PFA, at 40 °C

Run	Molar ratios	$k_4^{org} (\times 10^5 \text{ l}^2/(\text{mol}^2 \text{ min}))$	$k_5^{org} (\times 10^3 \text{ l}^2/(\text{mol}^2 \text{ min}))$
Deg-1	epFAME/FA = 1/0.3	6.0 ± 0.13	–
Deg-2	epFAME/FA = 1/0.5	5.6 ± 0.26	–
Deg-3	epFAME/H ₂ O/FA = 1/1.1/0.3	6.5 ± 0.10	–
Deg-4	epFAME/H ₂ O/FA = 1/1.1/0.5	6.0 ± 0.096	–
Deg-5	epFAME/H ₂ O ₂ /FA = 1/1.1/0.3	6.5 ± 0.10	2.2 ± 0.36
Deg-6	epFAME/H ₂ O ₂ /FA = 1/2.0/0.3	6.5 ± 0.10	4.4 ± 0.77
Deg-7	epFAME/H ₂ O ₂ /FA = 1/5.0/0.3	6.5 ± 0.10	5.6 ± 0.48
Deg-8	epFAME/H ₂ O ₂ /FA = 1/2.0/0.5	6.0 ± 0.096	5.1 ± 0.20
Deg-9	epFAME/H ₂ O ₂ /FA = 1/2.0/1	6.0 ± 0.096	N.A. ^a

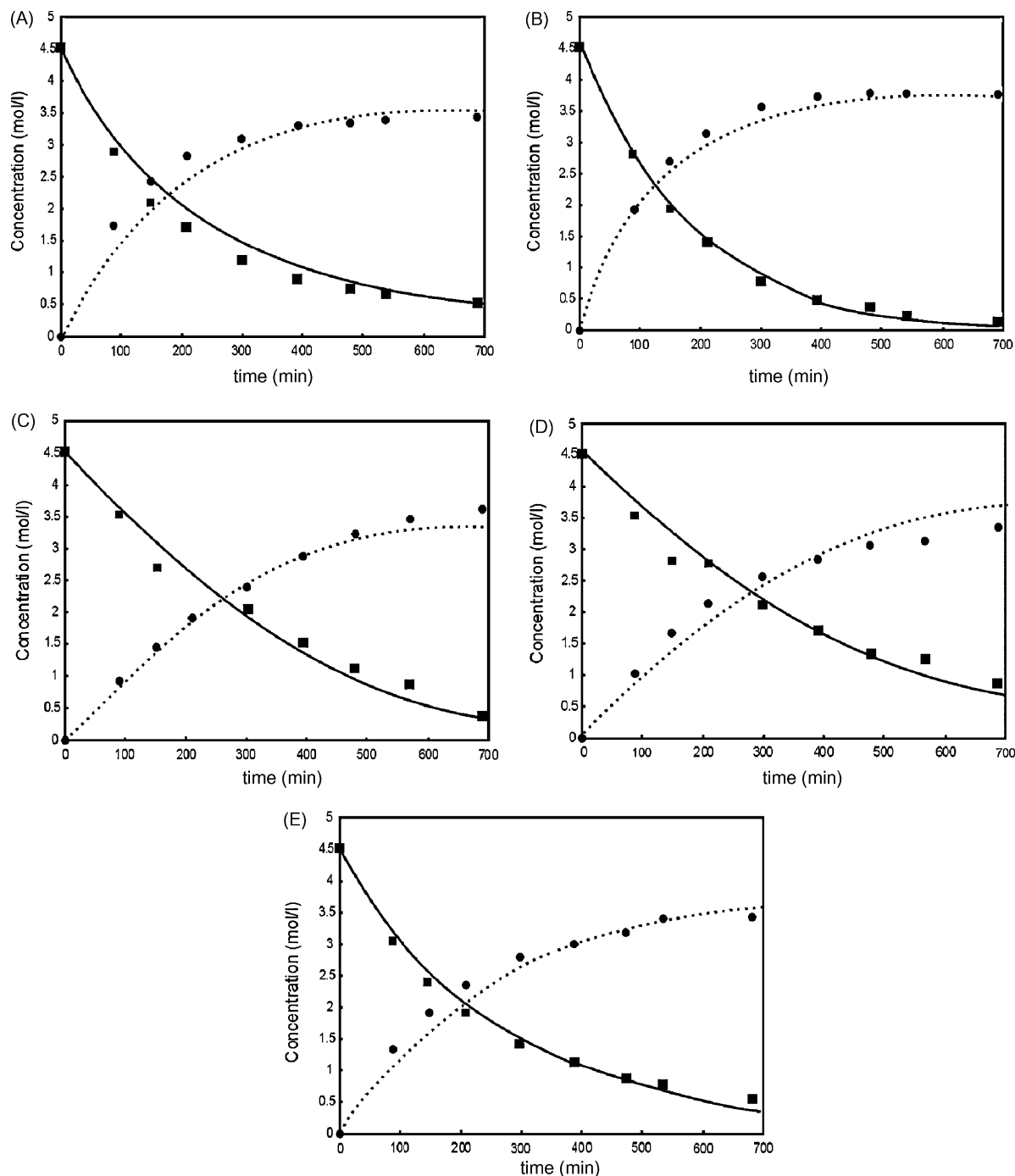
^a Ring-opening reaction under the fast kinetic regime [10].**Fig. 5.** Experimental vs. model (simulated) molar concentration of double bonds (mol C=C/l) and epoxide groups (mol Ep/l) vs. time, during the epoxidation. Markers are experimental data, curves are model predictions. Plots in (A), (B), (C), (D) and (E) correspond to runs Ep-3, Ep-5, Ep-6, Ep-7 and Ep-11 listed in Table 1, respectively.

Table 8

Reaction rate constant (individual runs) corresponding to the epoxidation of soybean FAME with performic acid generated *in situ*, from formic acid and H₂O₂(aq.), at 40 °C

Run	Molar ratios C=C/H ₂ O ₂ /FA	k_3^{org} ($\times 10^2$ l/(mol min))
Ep-3	1/1.1/0.5	4.7 $\pm$ 0.21
Ep-5	1/2/0.5	4.2 $\pm$ 0.18
Ep-6	1/1.1/0.3	3.8 $\pm$ 0.11
Ep-7	1/5/0.3	3.1 $\pm$ 0.34
Ep-11	1/2/0.3	3.6 $\pm$ 0.23

between acetic and formic acids, and assuming that the same (second) reaction order applies in the case of FA and PFA, Eq. (20) can be rewritten as

$$R_i^{\text{org}} = k_i^{\text{org}}([I]^{\text{org}})^2([Ep]^{\text{org}}) \quad (21)$$

Indeed, these equations were already introduced above, within the set of Eqs. (1)–(19), without explicit justification. The reaction rate constant k_4^{org} was found for each of the individual experimental runs Deg-1 to Deg-4 indicated in Table 2. This rate constant was then employed to obtain k_5^{org} for runs Deg-5 to Deg-9. The reaction rate constants were obtained by using Euler's numerical method in the MATLAB package, employing the Nelder–Mead algorithm [25], by minimizing the differences (least squares method) between the experimental vs. predicted values of concentrations.

4.3. Kinetic modelling results

Table 7 gives the obtained values of k_4^{org} and k_5^{org} for each of the individual degradation runs. Both of them are fairly constant, thus validating the equilibrium two-phase model used here. Also, it can be promptly appreciated that the attack on the epoxide ring by either 'neat' or solvated FA is just about equal. Lastly, it is worth noticing that the k_4^{org} kinetic rate constant has the same order of magnitude than that of solvated acetic acid [10] and that the attack on the oxirane groups by the peracid (PFA) is much more intense than the one of the corresponding carboxylic acid (FA): $k_5^{\text{org}}/k_4^{\text{org}} \approx 80$ -fold, in similar fashion as in the case of peracetic vs. acetic acids, respectively.

The kinetic rate constant for the epoxidation of the double bonds by PFA in the organic phase (k_3^{org}) was calculated by solving the set of simultaneous ODEs using Euler's numerical method in MATLAB, as above, for each of the experimental runs Ep-3, Ep-5 to Ep-7 and Ep-11 indicated in Table 1 ($T = 40$ °C). The corresponding calculated values are listed in Table 8. Fig. 5 plots the experimental concentration values of double bonds and epoxide groups vs. time on these runs, together with the simulated ones, using an average value of $k_3^{\text{org}} = 3.88 \times 10^{-2}$ l mol⁻¹ min⁻¹. Both fits are fair.

These k_3 values are similar to those found by La Scala and Wool [3], who used preformed performic acid at 20 °C to epoxidized different fatty acid methyl esters. However, they did not include the degradation of the oxirane ring in their reaction model.

While trying to maximize oxirane selectivity and yield, several refined vegetable oils were epoxidized with formic acid at 40 °C using a large excess of H₂O₂ (30 wt%) and adding benzene (molar ratio C=C/benzene = 1/5) as a diluent (or 'ring-integrity preserver'). Table 6 shows that in every case these goals were achieved. So, to further exploit the equilibrium two-phase model presented hereby, the kinetic rate constant (k_3^{org}) associated with the epoxidation of sunflower oil was calculated using the set of ODEs, but excluding any of the ring-opening reactions. Fig. 6 compares the excellent fit between the experimental and simulated concentration vs. time data of [C=C]^{org} and [Ep]^{org}. As before, k_1^{aq} and k_2^{aq} were calculated using Rangarajan et al.'s data [1]. At this temperature, the calculated value of k_3^{org} was 0.0016 ± 0.00024 l mol⁻¹ min⁻¹; which is of an order of magnitude lower than the previously calculated

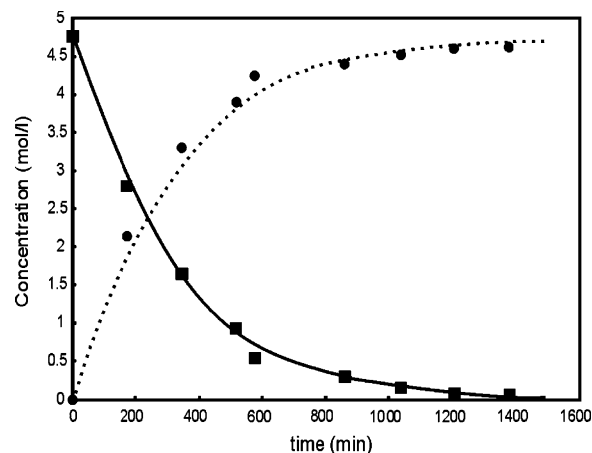


Fig. 6. Epoxidation of refined sunflower oil with PFA generated *in situ* using benzene as diluent. Markers are experimental data, curves are model predictions. Process conditions are given in Table 6.

and entirely compatible with the diluting-moderating action of the added solvent.

5. Conclusions

In the epoxidation of soybean fatty acid methyl esters with PFA generated *in situ* from FA using highly concentrated hydrogen peroxide (up to 60 wt%) and moderate temperature (preferably 40 °C), the impact of temperature increases is significantly detrimental for achieving high yields and/or high oxirane-number. Higher concentrations of either formic acid or hydrogen peroxide are also harmful (particularly, the carboxylic acid) but much less than temperature.

Nevertheless, this process alternative compares favourably to the conventional one, which is conducted at 60 °C using 30 wt% H₂O₂; higher double bond conversion combined with high epoxide productivity and excellent selectivity are attainable.

Using economically sound FA-to-double bonds and H₂O₂-to-double bonds molar ratios, under well-mixed regimes, in which the immiscible polar and organic phases are always well dispersed, the epoxidation process can be adequately described using an (equilibrated) two-phase reaction model accounting for just the reversible peracid formation (in the aqueous phase) and the epoxidation reaction proper, together with the attacks on the epoxide ring by FA and PFA (in the organic phase).

Acknowledgments

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Kinetics of *in situ* Epoxidation of Soybean Oil in Bulk Catalyzed by Ion Exchange Resin

Snežana Sinadinović-Fišer^a, Milovan Janković^a, and Zoran S. Petrović^{b,*}

^aFaculty of Technology, University of Novi Sad, Novi Sad, Yugoslavia, and ^bKansas Polymer Research Center, Pittsburg State University, Pittsburg, Kansas 66762

ABSTRACT: The kinetics of the epoxidation of soybean oil in bulk by peracetic acid formed *in situ*, in the presence of an ion exchange resin as the catalyst, was studied. The proposed kinetic model takes into consideration two side reactions of the epoxy ring opening involving the formation of hydroxy acetate and hydroxyl groups as well as the reactions of the formation of the peracid and epoxy groups. The catalytic reaction of the peracetic acid formation was characterized by adsorption of only acetic acid and peracetic acid on the active catalyst sites, and irreversible surface reaction was the overall rate-determining step. Kinetic parameters were estimated by fitting experimental data using the Marquardt method. Good agreement between the calculated and experimental data indicated that the proposed kinetic model was correct. The effect of different reaction variables on epoxidation was also discussed. The conditions for obtaining optimal epoxide yield (91% conversion, 5.99% epoxide content in product) were found to be: 0.5 mole of glacial acetic acid and 1.1 mole of hydrogen peroxide (30% aqueous solution) per mole of ethylenic unsaturation, in the presence of 5 wt% of the ion exchange resin at 75°C, over the reaction period of 8 h.

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KEY WORDS: Epoxidation, ion exchange resin, *in situ*, kinetics, reaction parameters, soybean oil.

Although numerous references exist in the literature concerning the methods of epoxidation of different olefinic substrates, many fewer are concerned with the kinetics of epoxidation. The kinetics of the process depend on the reaction conditions. Epoxidation of vegetable oils can be carried out in solution or in bulk, with *in situ* (1–3) formed or preformed peracids (4–9), with homogeneous or heterogeneous catalysts.

A kinetic model for *in situ* epoxidation of anchovy oil with partially preformed peracetic acid in the presence of a resin catalyst was reported (10). In the range of the operating variables, epoxidation and ring opening were described by a pseudo first-order reaction, applying the principle of the stationary state. Two studies of the kinetics of the *in situ* epoxidation of oleic acid with hydrogen peroxide and acetic acid and of methyl esters of palm olein by performic and peracetic acid, both carried out in the presence of sulfuric acid as a

catalyst, concluded that the rate-determining step of the epoxidation process was the formation of peracetic (or performic) acid (11,12). Rangarajan *et al.* (13) reported kinetic parameters for the *in situ* epoxidation of soybean oil by peracetic acid, again in the presence of sulfuric acid as the catalyst, but treated it as a two-phase system. Significantly higher rates were obtained when heat and mass transfer limitations were removed. The proposed model also predicted the effect of the addition of an inert solvent on epoxidation.

With an acidic ion exchange resin as the catalyst for the epoxidation of vegetable oils, the porous structure of the solid catalyst and the size of the natural unsaturated triglycerides were found to minimize side reactions and thus improve selectivity (SE) (14). The presence of an inert solvent in the reaction mixture appeared also to stabilize the reaction of epoxidation and minimize side reactions, such as the opening of the epoxy ring, especially at higher temperatures (12).

Since the ion exchange resin has the same effect as a solvent, it is reasonable to assume that the epoxidation of soybean oil may be carried out in bulk with a high SE, i.e., in the absence of an inert solvent, as we did in the present work. We also carried out the epoxidation in solution to confirm our assumptions, but the emphasis was on the study of the effects of reaction variables on conversion of double bonds and epoxy yield during epoxidation of soybean oil in bulk. The reaction was conducted with peracetic acid formed *in situ* from acetic acid and hydrogen peroxide in the presence of an ion exchange resin as a catalyst. Thus, the epoxidation that we studied was a heterogeneous catalytic process characterized by the presence of a solid phase (catalyst), an aqueous phase (acetic acid, hydrogen peroxide, and water), and an oil phase. The kinetics of such a system is very complex even for the simple first-order reactions, and some assumptions such as Langmuir-Hinshelwood-Hougen-Watson postulates may help to simplify the rate equations (15).

The objective of this work was to develop, on the basis of the experimental data, a kinetic model for the heterogeneous catalytic system that describes the course of epoxidation of soybean oil in bulk, with *in situ* formed peracetic acid and an acid ion exchange catalyst. The adopted method involved the definition of possible kinetic models for different chemisorption mechanisms, their mathematical description, testing of the models by solving the system of differential equations, selection of the viable one, and comparison of the experimental data with the calculated values from the accepted model.

*To whom correspondence should be addressed at Kansas Polymer Research Center, Pittsburg State University, 1501 S. Joplin St., Pittsburg, KS 66762. E-mail: zpetrovi@pittstate.edu

EXPERIMENTAL PROCEDURES

Materials. Soybean oil with an iodine value of 130 (Hanus) was kindly supplied by "Servo Mihalj" Zrenjanin, Yugoslavia. Glacial acetic acid (>99.5%), hydrogen peroxide (30% water solution), and analytical grade benzene were used. Ion exchange resins Amberlite IR-120 from Rohm & Hass Co. (Philadelphia, PA) and Dowex 50X from Dow Chemical Co. (Midland, MI) were used in their acid form.

Methods. The epoxidation of soybean oil was carried out with peracetic acid generated *in situ*. The reaction conditions and the properties of the products are listed in Table 1. The procedure involved adding 100 g of soybean oil (0.5122 mole of ethylenic unsaturation), dissolved in glacial acetic acid and benzene (20 wt% of the soybean oil), into a 500-mL three-necked reactor, equipped with a reflux condenser, thermometer, and dropping funnel. The ion exchange resin was first added to the reactor. The amount of the applied dry ion exchange resin was expressed in percentages of the sum of the weights of the acetic acid and hydrogen peroxide used, as well as a percentage of the soybean oil weight. Cooling of the reaction mixture was maintained with the water bath and agitation with a magnetic stirrer. The temperature was kept to within $\pm 1^\circ\text{C}$, and the stirring rate was controlled (1000 rpm) so that a fine dispersion of oil was achieved. At the beginning, the mixture was heated to 50°C , and the hydrogen peroxide solution was added incrementally over a half-hour period while maintaining the reaction temperature at 50°C . Then the temperature of the reaction mixture was allowed to rise to the desired level. The reaction was followed by withdrawing and analyzing 5-mL samples of the reaction mixture at defined time intervals.

After a certain time (12 to 24 h), when the iodine value of the substrate had been reduced enough, the resin was separated from the cooled reaction mixture by filtration. If the ion exchange resin was to be reused, it was washed with ether and dried. Upon cooling, the reaction mixture separated into water and oil layers. The oil layer was washed several times with warm water ($30\text{--}35^\circ\text{C}$) until it was acid-free. The remaining traces of water and benzene (if used) were removed under a reduced pressure at $60\text{--}70^\circ\text{C}$. Every sample of the reaction mixture followed the same separation procedure described above. The products and the samples were analyzed for the iodine and epoxy oxygen (EO) values and viscosity. The Hanus method for iodine number (IO) (16) and standard HBr-acetic acid method (17) for EO content determinations were used.

RESULTS AND DISCUSSION

Effects of the reaction variables. The effect of reaction variables on the epoxidation was studied. The variables were: molar ratio of the reactants (ethylenic unsaturation of oil/acetic acid/hydrogen peroxide), the type of catalyst and catalyst concentration, temperature, and presence of an inert solvent, as well as the possibility of reusing the ion exchange resin. The values of reaction variables and product properties are shown in Table 1 only for the maximum epoxy oxygen contents ($\text{EO}_{e,m}$, where *e* indicates experimentally determined value and *m* indicates maximum value) reached in each synthesis.

The amount of hydrogen peroxide used for the epoxidation of soybean oil was always kept at 1.1 moles per mole of ethylenic unsaturation of oil. For the sample with a maximal content of EO, the concentration of unreacted hydrogen per-

TABLE 1
Values of Reaction Variables and Product Properties for the Maximal Content of Epoxy Oxygen Reached in Each Run of the *in situ* Epoxidation of Soybean Oil by Peracetic Acid in the Presence of the Ion Exchange Resin as Catalyst^a

Synthesis no.	Molar ratio Unsat./CH ₃ COOH/H ₂ O ₂			Amberlite ^b (wt%)	T (°C)	Benzene (wt%)	t (h)	Iodine number ^c (IN _e)	Conversion ^d X (%)	Epoxy oxygen ^e (EO _{e,m}) %	Yield ^f RYE (%)	Selectivity ^g (SE)	Viscosity η (mPa·s)
S1	1	1	1.1	5[4.73]	75	20	6	3.7	97.7	5.88	77.65	0.79	853.3
S2	1	5	1.1	5[10.88]	75	20	1	71.0	45.4	2.8	36.97	0.81	1462.4
S3	1	0.5	1.1	5[3.96]	75	20	8	11.0	91.5	6.02	79.48	0.87	527.7
S4	1	0.5	1.1	5[3.96]	60	—	10	17.2	86.8	5.68	74.99	0.86	444.3
S5	1	0.5	1.1	5[3.96]	30	—	24	35.0	73.1	3.70	48.85	0.67	285.6
S6	1	0.5	1.1	15[11.89]	75	—	7	4.0	96.9	6.24	82.39	0.85	577.9
S7	1	0.5	1.1	2[1.28]	75	—	12	12.3	75.2	5.01	66.15	0.88	309.5
S8	1	0.5	1.1	5[3.96]	75	—	8	11.5	91.1	5.99	79.09	0.87	522.7
S9	1	0.5	1.1	5 [3.96] (2x)	75	—	8	11.5	91.1	5.89	77.77	0.85	523.8
S10	1	0.5	1.1	5[3.96] (5x)	75	—	9	10.2	92.15	5.76	76.05	0.32	548.9
S11	1	0.5	1.1	5[3.96] ^h	75	—	9	13.4	89.7	5.94	78.42	0.87	519.5

^aFor IN₀ = 130 and EO_t = 7.574% (see below).

^bAmberlite IR-120 (Rohm & Hass Co., Philadelphia, PA). Numbers in brackets represent the concentration expressed in percentages of oil weight.

^cIodine number, determined experimentally according to Reference 16.

^dConversion X(%), conversion of double bonds as related to IN₀ (the initial IN). Calculated as $X = [(IN_0 - IN)/IN_0] \cdot 100$.

^eEO_{e,m}(%) experimentally determined maximal content of epoxy oxygen in 100 g of oil.

^fRYE (%), relative yield of epoxides, calculated as $RYE = 100 \cdot EO_e/EO_t$. EO_t is defined as the theoretical maximum content of epoxy oxygen in 100 g of oil, calculated as $EO_t = \{(IN_0/2A_1)/[100 + (IN_0/2A_1) \cdot A_0]\} \cdot A_0 \cdot 100$, where $A_1 = 126.9045$ and $A_0 = 16.0000$.

^gSE, relative yields of epoxides, calculated from the conversion of double bonds, as $SE = EO_e \cdot IN_0/EO_t (IN_0 - IN)$.

^hDowex 50X (Dow Chemicals, Midland, MI).

oxide in the reaction mixture was 7.8% for the molar ratio of ethylenic unsaturation of oil/acetic acid/hydrogen peroxide = 1:0.5:1.1 (synthesis S8), coming close to the equilibrium concentration.

The effect of the acetic acid molar ratios on the epoxidation was studied by using 1, 5, and 0.5 moles of acid per mole of ethylenic unsaturation (syntheses S1, S2, and S3, respectively). Variation of both IN_e and EO_e with time is presented in Figure 1. A higher molar ratio of acetic acid to ethylenic unsaturation increased the reaction rate and the ratio of side reactions. Thus, the use of a higher molar ratio of acetic acid during *in situ* epoxidation reduced the yield of epoxy groups. The maximal yield of the epoxy groups was achieved when 0.5 mole of acetic acid per mole of ethylenic unsaturation was used.

The catalytic effect of the ion exchange resin was investigated by using 2, 5, and 15 wt% of Amberlite IR 120 (syntheses S7, S8, and S6, respectively). With an increasing concentration of the catalyst, the reaction rate and the epoxy yield increased. At the same time, the ratio of the side reactions related to the conversion of double bonds increased from 12 to 15% (SE decreased from 0.88 to 0.85). Since the maximal yield of epoxide groups, obtained with 5 wt% of the catalyst, was only 3.3% lower than those achieved with 15%, the optimal quantity of the catalyst was selected to be 5%. The effect of the catalyst concentration on the course of epoxidation is shown in Figure 2.

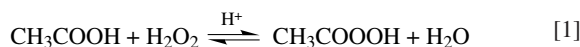
Using two strong ion exchange resins of the sulfonated polystyrene type, Amberlite IR-120 and Dowex 50X, for the epoxidation of soybean oil in bulk produced no significant difference in the maximal epoxy oxygen content (syntheses S8 and S11).

The influence of temperature (T) on the course of epoxidation was investigated by carrying out the reaction at 30, 60, and 75°C (syntheses S5, S4, and S8). Variation of IN and EO content with reaction time is displayed in Figure 3. The reac-

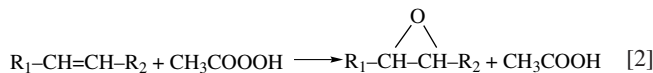
tion rate, conversion of double bonds (X), relative epoxy yield (RYE), and SE were found to increase with increasing temperature. At the highest temperature, the shortest reaction time (t) was obtained, and the maximal EO content of 5.99% was reached. Since the same relative epoxy yield but somewhat lower SE was obtained at 78°C (data not shown), the optimal temperature was selected to be 75°C.

Plots (not shown) of the change in IN and EO contents with time for syntheses S3 (with benzene) and S8 (the same parameters of epoxidation, but without benzene) showed no significant difference between the two. The presence of the solvent was not deemed necessary, since the relative epoxy yield was not significantly higher and the ratio of side reactions was the same (i.e., the SE in Table 1) when benzene was used.

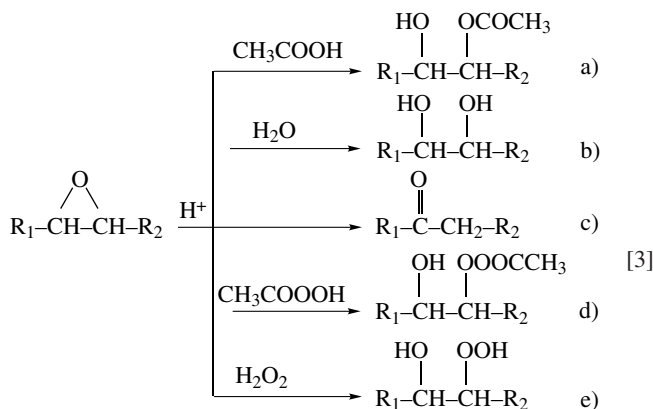
Model selection. *In situ* epoxidation of soybean oil with peracetic acid in the presence of an ion exchange resin is a heterogeneous catalytic process in which peracetic acid formation is an acid-catalyzed reaction:



whereas the main reaction involving the epoxy group formation is an uncatalyzed reaction:



The following side reactions of the epoxy ring cleavage that may take place are acid-catalyzed:



To reduce the number of model parameters, i.e., to simplify the mathematical model, which represents the system of differential equations for rates of the reactions shown above, heat and mass diffusion resistances in the system liquid–solid are usually ignored (15,18). Since the stirring was good and the epoxidation was conducted isothermally, those diffusion resistances were assumed to be negligible and the steps concerning the transport phenomena in our studies of kinetics were also ignored. Thus, the formulation of equations for the overall rates for catalyzed reactions of peracetic acid formation (reaction 1) and epoxide ring opening reactions (reactions 3) in such a case takes into consideration only the reaction on the solid catalyst, i.e., chemisorption. The reaction

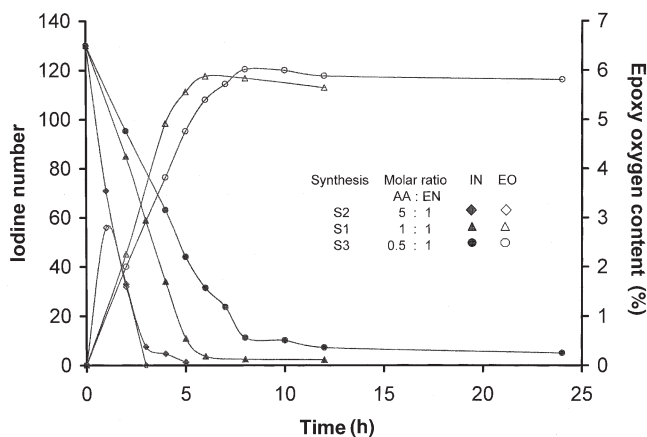


FIG. 1. Effect of different molar ratios of acetic acid (AA) to ethylenic unsaturation (EN) of oil on the *in situ* epoxidation of soybean oil in benzene (20 wt%) with 1.1 moles of 30% hydrogen peroxide at 75°C, and in the presence of 5% of Amberlite IR 120 (Rohm & Hass Co., Philadelphia, PA). IN , iodine number; EO , epoxy oxygen content.

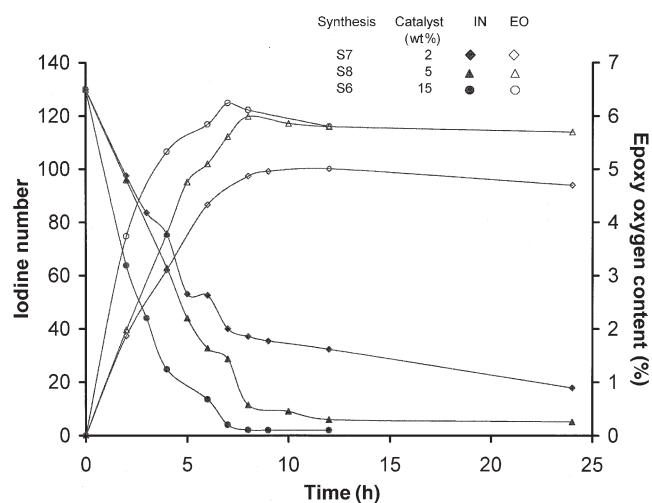


FIG. 2. Effect of the amount of catalyst on *in situ* epoxidation of soybean oil in bulk at 75°C, with molar ratio of ethylenic unsaturation of oil/acetic acid/hydrogen peroxide (30%) = 1:0.5:1.1. For abbreviations see Figure 1.

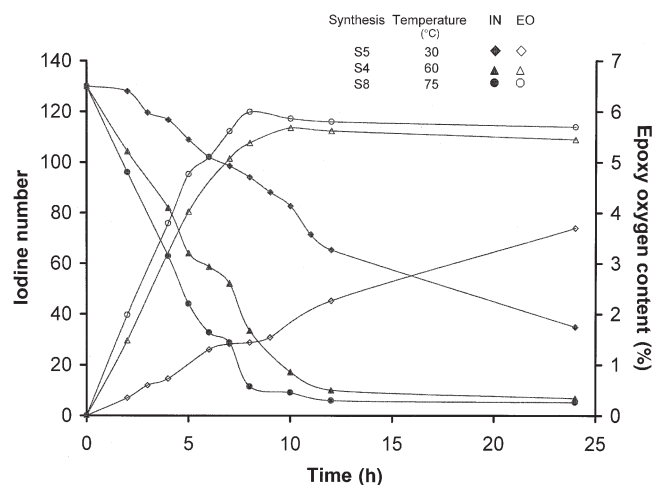


FIG. 3. Influence of temperature on *in situ* epoxidation of soybean oil in bulk with 1.1 moles of hydrogen peroxide (30%) and 0.5 mole of acetic acid in the presence of 5% of Amberlite IR 120. For abbreviations and company source, see Figure 1.

TABLE 2
Specifications of Assumptions for the Selected Kinetic Models^a

Model no.	Reaction ^b taken into consideration				Chemisorption					
					Adsorption		Reversible			
					Dissociation				Irreversible	Determining step
	Homogeneous	Order	Heterogeneous	Order	Without	With			Order	
1	1,2,3a,3b	1	—	—	—	—	—	—	—	—
2	1,2,3a,3b,3c	1	—	—	—	—	—	—	—	—
3	1,2,3a,3b	^b	—	—	—	—	—	—	—	—
4	2,3a,3b	1	1	—	AA, H ₂ O ₂ , PAA, H ₂ O	—	All steps	—	1	Adsorption of AA
5	2,3a,3b	1	1	—	AA, PAA	—	All steps	—	1	"
6	2,3a,3b	1	1	—	AA, PAA	—	All steps	—	^d	"
7	2,3a,3b	1	1	—	AA, PAA	—	Adsorption, desorption	Surface reaction	1	"
8	2,3a,3b	1	1	—	AA, H ₂ O ₂ , PAA, H ₂ O	—	All steps	—	1	Desorption of PAA
9	2,3a,3b	1	1	—	AA, PAA	—	All steps	—	1	"
10	2,3a,3b	1	1	—	AA, PAA	—	All steps	—	^d	"
11	2,3a,3b	1	1	—	AA, PAA	—	Adsorption, desorption	Surface reaction	1	"
12	2,3a,3b	1	1	—	AA, H ₂ O ₂ , PAA, H ₂ O	—	All steps	—	1	Surface reaction
13	2,3a,3b	1	1	—	AA, PAA	—	All steps	—	1	"
14	2,3a,3b	1	1	—	AA, PAA	—	All steps	—	^d	"
15	2,3a,3b,3c	1	1	—	AA, PAA	—	All steps	—	^d	"
16	2,3a-d	1	1	—	AA, PAA	—	All steps	—	^d	"
17	2,3a,3b	1	1	—	AA, PAA	—	Adsorption, desorption	Surface reaction	1	"
18	2,3a,3b	1	1	—	AA, PAA	—	Adsorption, desorption	Surface reaction	^d	"
19	2,3a,3b	1	1	—	AA	—	Adsorption	Surface reaction	1	Surface reaction
20	2	1	1	—	AA, H ₂ O ₂ , PAA, H ₂ O	—	All steps	—	1	Surface reaction
21	2	1	3a	—	EO, S	—	All steps	—	1	Surface reaction
			1	—	AA, PAA	—	All steps	—	1	Surface reaction
			3a	—	EO, S	—	All steps	—	1	Surface reaction
22	2	1	1	—	AA, PAA	—	Adsorption, desorption	Surface reaction	1	Surface reaction
			3a	—	EO, S	—	All steps	—	1	Surface reaction
			1	—	AA, PAA	—	All steps	—	1	Surface reaction
23	2	1	1	—	AA, PAA	—	Adsorption, desorption	Surface reaction	1	Surface reaction
			3a	—	EO, S	—	All steps	—	1	Surface reaction
			1	—	AA, PAA	—	All steps	—	1	Surface reaction
24	2	1	1	—	AA, PAA	—	Adsorption	Surface reaction	1	Surface reaction
			3a	—	EO	—	Adsorption	Surface reaction	1	Surface reaction

^aAA, acetic acid; PAA, peracetic acid; EN, ethylenic unsaturation of oil; EO, epoxy oxygen; S, side reaction products.

^bReactions are enumerated in text.

^cThe assumed order for all reactions is 1, except for homogeneous reactions in model 3, where the reaction order to the left is different from that to the right.

^dSurface reaction is zero order to H₂O₂ and H₂O.

TABLE 3
Values of Calculated Kinetic Parameters^a for Models No. 13 and 17

Model No. 13		Model No. 17	
$C_i k_{sr}$	i.e., $p_1 = 2.163$	$C_i k_{sr}$	i.e., $p_1 = 2.263$
$K = (K_{AA} K_{SR})/K_{PAA}$	i.e., $p_2 = 2.048 \cdot 10^7$	K_{PAA}	i.e., $p_2 = 49.706$
k_3	i.e., $p_3 = 2.897$	k_3	i.e., $p_3 = 2.765$
k_4	i.e., $p_4 = 0.250$	k_4	i.e., $p_4 = 0.247$
k_5	i.e., $p_5 = 1.170 \cdot 10^{-4}$	k_5	i.e., $p_5 = 3.073 \cdot 10^{-4}$
K_{AA}	i.e., $p_6 = 0.9635$	K_{AA}	i.e., $p_6 = 0.973$
K_{PAA}	i.e., $p_7 = 50.151$		

^a $C_i k_{sr}$, concentration of active site per unit mass of catalyst (mol/g catalyst) $\times$ coefficient of surface reaction rate; K_{AA} , K_{PAA} , adsorption equilibrium constants; K_{SR} , equilibrium constant of surface reaction; the units for k_3 , k_4 , and k_5 , are (100 g oil)/s-mol).

proceeds on active sites of the catalyst surface in three steps: (i) adsorption of at least one of the reactants on the catalytic active site, (ii) surface chemical reaction between adsorbed atoms or molecules, or between adsorbed and not adsorbed reactants, and (iii) desorption of the products. Consequently, an overall rate equation for such a liquid–solid catalytic reaction is derived by estimating the rate equations for the individual steps, i.e., for adsorption, surface chemical reaction and desorption, and combining them to eliminate unknown surface concentrations. In this work we have adopted Langmuir-Hinshelwood-Hougen-Watson's approach for the development of the overall reaction rate equations (15). This approach reduces the number of rate coefficients (k) for individual steps and the number of equilibrium constants (K) in the overall reaction rate equation.

The next step for the simplification of the overall reaction rate equation is to assume that only one step is determining, while the other two proceed under nearly equilibrium conditions. Depending on which of the three steps controls the overall catalyzed reaction rate, it is possible, for the same assumed chemisorption mechanism, to select several kinetic expressions. If an assumption that one or all reactants/products may adsorb on active catalyst sites is also taken into consideration, the number of selected kinetic mechanisms, and thus kinetic equations for the overall catalytic reaction rate, rapidly increases.

The procedure for selecting the kinetic models in this work required choosing which reactions of the epoxidation process to consider, which are homogeneous (i.e., pseudohomogeneous) and which heterogeneous, the order of reactions, and chemisorption mechanism for heterogeneous reactions. The last-named choice refers to which reactants and/or products are adsorbed, how reactants/products are adsorbed (with or without dissociation), the reversibility or irreversibility of the steps, the order of the steps, and which step is rate-determining. Table 2 shows 24 selected kinetic models with specification of assumptions.

As was mentioned previously, the form of the kinetic equation may be different for the same chemisorption mechanism depending on which step is assumed to be rate-determining. According to the Langmuir-Hinshelwood-Hougen-Watson postulates, kinetic equations for the reactions catalyzed by a

solid are written as the combination of three groups:

$$(\text{kinetic factor})(\text{driving-force group})/(\text{adsorption group}) \quad [4]$$

The summary of expressions for these groups for various kinetic schemes is given in the literature (15). Different kinetic expressions for various assumptions concerning chemisorption resulted in different mathematical models. Each mathematical model represents a system of differential equations that mathematically describes the whole process of epoxidation. Their solution gives parameters (p_i), i.e., the concentration of active site per unit mass of catalyst, coefficients of reaction rates (k_i) and equilibrium constants (K_i) for the adsorption or desorption step, or their combinations. The inputs were experimentally determined concentrations of a reactant ($[EN]_e$) and a product ($[EO]_e$). The parameters were estimated by fitting experimental data using the Marquardt method (19). Twenty-three experimental data points (see Fig. 4) were used to fit three to eight parameters. The number of parameters varied and depended on the selected model. The Runge-Kutta method was applied for solving the system of differential equations.

Once the model parameters had been calculated, the viable model was chosen on the basis of the parameter values. Since all parameters have physical meaning, they cannot be of negative or impossible values. All selected models that gave negative values of only one parameter, or negative calculated values of reactant and/or product concentrations, were rejected. Only model Nos. 13 and 17 had positive values for all parameters and gave positive calculated values of reactant and product concentrations. Values of calculated model parameters (p_i) for both models are presented in Table 3.

In model No. 13, the high value of parameter p_2 , i.e., the equilibrium constant K , which is the consequence of the high value of the equilibrium constant of surface reaction (K_{SR} , calculated as 1.066×10^9), indicates that the surface reaction proceeds in only one direction, to the right. That is confirmed in model No. 17, where the catalytic reaction of peracetic acid for-

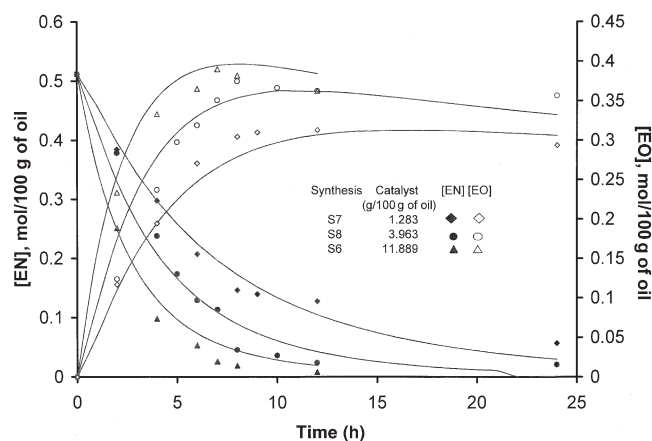
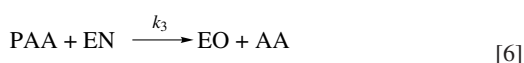
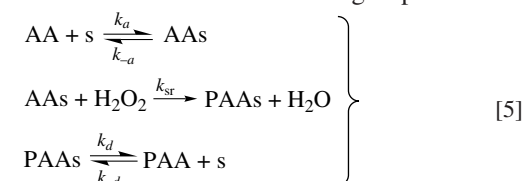


FIG. 4. Time dependence of experimentally determined (points) and calculated (solid curves) concentrations of ethylenic unsaturation of oil [EN] and epoxy oxygen [EO] for the *in situ* epoxidation of soybean oil in bulk at 75°C, with 1.1 moles of hydrogen peroxide (30%) and 0.5 mole of acetic acid, in the presence of different amounts of Amberlite IR 120. See Figure 1 for company source.

mation on the surface was supposed to be irreversible. The symbols K_{AA} and K_{PAA} refer to the adsorption equilibrium constants of acetic acid and peracetic acid, respectively. Notice that in both models the parameter p_1 is the combination of the coefficient of the surface reaction rate (k_{sr}) and the unknown concentration of active catalyst sites (C_t) where t represents "total."

Accepted model. The accepted kinetic model No. 17 assumes that in the catalytic reaction of the peracetic acid formation (1), only acetic (AA) and peracetic (PAA) acids are adsorbed on the active catalytic site(s) and that irreversible surface reaction is the overall rate-determining step:



where letter subscripts in the rate coefficients (k_i) indicate adsorption (a), surface reaction (sr), and desorption (d). AAs and PAAs describe adsorbed acetic acid (AA) and peracetic acid (PAA) on s, EN is the ethylenic unsaturation of soybean oil, EO is epoxy oxygen, and S is the product of the side reaction.

The corresponding mathematical model may be represented by the following equations:

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = -\frac{M_k C_t k_{sr} K_{AA} [\text{AA}] [\text{H}_2\text{O}_2]}{1 + K_{AA} [\text{AA}] + K_{PAA} [\text{PAA}]} \quad [8]$$

$$\frac{d[\text{AA}]}{dt} = \frac{d[\text{H}_2\text{O}_2]}{dt} + k_3 [\text{PAA}] [\text{EN}] - k_4 [\text{EO}] [\text{AA}] \quad [9]$$

$$\frac{d[\text{PAA}]}{dt} = -\frac{d[\text{H}_2\text{O}_2]}{dt} - k_3 [\text{PAA}] [\text{EN}] \quad [10]$$

$$\frac{d[\text{EN}]}{dt} = -k_3 [\text{PAA}] [\text{EN}] \quad [11]$$

$$\frac{d[\text{EO}]}{dt} = k_3 [\text{PAA}] [\text{EN}] - k_4 [\text{EO}] [\text{AA}] - k_5 [\text{EO}] [\text{H}_2\text{O}] \quad [12]$$

$$\frac{d[\text{H}_2\text{O}]}{dt} = -\frac{d[\text{H}_2\text{O}_2]}{dt} - k_5 [\text{EO}] [\text{H}_2\text{O}] \quad [13]$$

$$\frac{d[\text{S}]}{dt} = k_4 [\text{EO}] [\text{AA}] + k_5 [\text{EO}] [\text{H}_2\text{O}] \quad [14]$$

where brackets are used to define the concentration of the reactants, M_k is the catalyst-to-oil ratio, and K_{AA} and K_{PAA} are the adsorption equilibrium constants for AA and PAA, respectively.

TABLE 4

Comparison of Experimentally Determined and Calculated Values of Time, IN, and EO for Maximal Yields of Epoxide, Reached in the *in situ* Epoxidation of Soybean Oil by Peracetic Acid, in the Presence of Different Quantities of the Ion Exchange Resin, at 75°C^a

Synthesis no.	Catalyst (wt%)	t_e (h)	IN _e	EO _{e,m} (%)	t_c (h)	IN _c	EO _c (%)
S7	2	12	12.3	5.01	15	16.92	5.01
S8	5	8	11.5	5.99	10	12.87	5.80
S6	15	7	4.0	6.24	8	9.23	6.34

^aSubscript e, experimental; subscript c, calculated; subscript m, maximal; for other abbreviations see Table 1.

The calculated parameters for the accepted model No. 17 are given in Table 3. This mathematical model fits well the experimental values of the measured variables: concentrations of ethylenic unsaturation of oil [EN] and [EO]. Figure 4 illustrates the results of the epoxidation of soybean oil by *in-situ* generated peracetic acid in bulk in the presence of different concentrations of Amberlite IR 120 applied as catalyst at 75°C. It shows the time change for both the experimentally determined values ([EN]_e and [EO]_e) and the calculated ones ([EN]_c and [EO]_c), as the points and solid curves, respectively.

Table 4 shows the numerical values of the IN and EO content calculated from the accepted model (IN_c and EO_c), together with the experimentally determined ones (IN_e and EO_e), all for the attained maximal yields of EO.

Although the experimental and calculated values of the maximal content of EO do not differ by more than 3.27% (for the synthesis S8), the differences between real and predicted reaction times to reach the maximum content of EO are significant. That may be explained by the difficulty in locating a precise maximum on experimental curves (see Fig. 2). Good agreement between experimental and calculated data indicates that the proposed model No. 17 is correct. It suggests that the catalytic reaction of peracetic acid formation may be considered irreversible, since the reaction of epoxy compound formation, involving consumption of peracetic acid, is fast enough ($k_3 > C_t k_{sr}$) and the equilibrium in the reaction of peracetic acid formation shifts to the right. Small rate coefficients (k_4 and k_5 in Table 3) for both side reactions (6a and 6b) indicate that the ring opening reactions do not occur to a significant extent. This is reflected in the high values of SE in Table 1 for all S6, S7, and S8 syntheses.

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THERMAL ANALYSIS OF SOYBEAN OIL BASED POLYOLS

B. Lin, L. Yang*, H. Dai, Q. Hou and L. Zhang

School of Chemistry and Environment, South China Normal University, Guangzhou P. R. China 510631

Soybean oil based polyols (5-OH polyol, 10-OH polyol and 15-OH polyol) were synthesised from epoxidized soybean oil. The melting peak of polyols and the relationship between melting peak and the number-average functionality of hydroxyl in polyols were investigated by differential scanning calorimetry (DSC). The thermal decomposition of polyols and some of their thermal properties by thermogravimetry (TG) and derivative thermogravimetry (DTG) were also studied. The thermal stability of polyols in a nitrogen atmosphere was very close hence they had a same baseplate of triglyceride for polyols. The extrapolated onset temperature of polyols in their thermal mass loss, first step had a decreasing order: 5-OH polyol > 10-OH polyol > 15-OH polyol due to the difficulty in forming multiple elements ring of them had the same order.

The thermal behavior of polyols under non-isothermal conditions using Friedman's differential isoconversional method with different heating rates indicated that the 5-OH polyol had the lowest activation energy in thermal decomposition amongst these polyols according to the same fractional mass loss because of the weakest intramolecular oligomerization. The 15-OH polyol was prior to reach the mass loss region because the six-member ring is more stable than the three-member ring from 10-OH polyol and more easily formed.

Keywords: Friedman's analysis, polyol, soybean oil, thermal stability, thermogravimetry

Introduction

Thermogravimetry as a thermoanalytical method presents many advantages as a result of its precision, sensitivity, expeditiousness, and the small sample amount required in each experimental test. In recent years, thermal analysis has been successfully used for the determination of physical properties and the study of chemical reaction [1–8]. On the other hand, the thermogravimetry technique is useful in the investigation of the thermal stability of vegetable oils and their derivatives [9, 10].

Soybean oil based polyol which is derivative of soybean oil; its thermal stability depends on its chemical structure with a high content of hydroxyl. This property is of great practical importance in avoiding the rupture of glyceryl chain of these polyols, especially when the polyol reacts with 2,4-toluene diisocyanate (TDI), 4,4'-methylenebis(phenyl isocyanate) (MDI), 1,6-hexamethylene diisocyanate (HDI) and other type of diisocyanate to produce polyurethane elastomers, foams and resins as these chemosynthesis reaction are drastic exothermic foaming reaction [11]. Soy oil based polyols of 5-OH polyol, 10-OH polyol and 15-OH polyol have some similarities in the TG and DTG curves due to the triglyceride as the same baseplate for polyols [6]. Thus, knowing the thermokinetic studies by thermogravimetry are very important in these formal

polyols. The acyl groups joined with the glyceryl short carbon chains present in the acylglyceride molecule was different in these formal polyols which would affect the detailed decomposition process [6].

Experimental

Materials

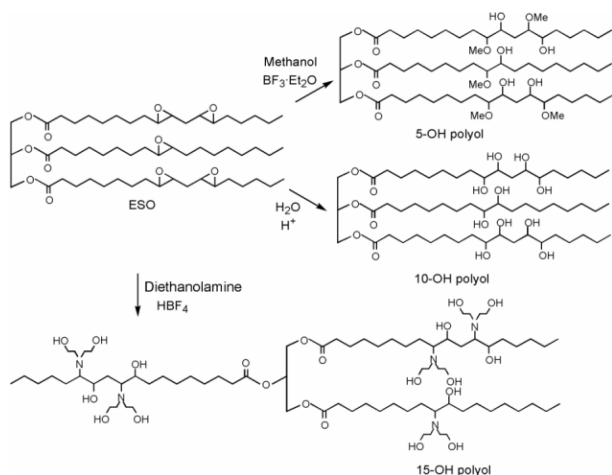
The epoxidized soybean oil (ESO) used in this research was kindly supplied by Nanhai Oil Co. Ltd. with a molecular mass of 985 (ESI-MS) and with a 4.375 mol kg⁻¹ epoxy oxygen content. Deuterated acetone (D, 99.9%) was supplied by Cambridge Isotope Laboratories, Inc., Andover, MA, USA. Diethanolamine [NH(CH₂CH₂OH)₂], methanol (CH₃OH), sulfuric acid (H₂SO₄), fluoboric acid (HBF₄), N,N-dimethylformamide (DMF), chloroform, isopropyl alcohol, potassium bromide (KBr) and sodium sulfate anhydrous (Na₂SO₄) were all analytically pure grade, and were purchased from Guangzhou Chemical Reagent Co. Ltd.

Synthesis of soy oil based polyols

Synthesis of 5-OH polyol

The definitely mass of aforementioned ESO (40.0 g) with 0.2 mass%, the BF₃·Et₂O was used as the cata-

* Author for correspondence: yanglt63@yahoo.com.cn; yanglt@scnu.edu.cn



Scheme 1 Idealized synthesis route of polyols

lyst, were both put in a four-necked reaction flask equipped with a reflux condenser and heated to the prearranged constant temperature ($40\pm 1^\circ\text{C}$) in a water bath with a mechanical stirrer for half an hour. Then 33.81 g methanol was added into the flask. Finally, the reaction mixture was heated up to $75\pm 1^\circ\text{C}$ for 6 h, at which point ammonia (30% in water, 2 mL) was added to quench the reaction. The product was washed with distilled deionised water until it was neutral to litmus and removed on a rotary evaporator with high vacuum equipment, and dried over anhydrous sodium sulfate. Finally the raw product was pressure-filtered. The product, a light-yellow viscous liquid, was isolated with a yield of 94%.

Synthesis of 10-OH polyol

The epoxy ring of ESO, when opened up under acidic conditions, will give a formal diol from each epoxy group. In a typical procedure, ESO (26.5 g) was mixed four times its mass (104 g) of 8% sulfuric acid solution in a 250 mL three-neck round-bottomed flask, fitted with a mechanical stirrer, thermometer, and reflux condenser. The sulfuric acid solution was added dropwise for 2 h and the reaction mixture was heated under reflux for 24 h while the reaction temperature was maintained at $70\pm 1^\circ\text{C}$. The product, extracted in chloroform, was then washed with distilled deionised water until neutral to litmus and dried over anhydrous sodium sulfate; finally the raw product was followed by pressure-filtered. The product, a pale yellow viscous liquid was isolated at 95% yield.

Synthesis of 15-OH polyol

For preparation of the 15-OH polyol, ESO and diethanolamine were reacted together at a reflux in the presence of isopropyl alcohol at $70\pm 1^\circ\text{C}$. In a typical procedure, ESO (25.4 g) was mixed with twice its

mass of isopropyl alcohol, with 2 g HBF_4 as the catalyst for opening reaction of epoxy ring of ESO, and a molar excess of diethanolamine (26.4 g) in a 250 mL three-neck round-bottom flask, fitted with a mechanical stirrer, thermometer, and reflux condenser. After 28 h, the isopropyl alcohol was removed from the product in a vacuum rotary evaporator. The product was separated and washed with distilled deionised water to completely remove excess diethanolamine. The raw product was dried over anhydrous sodium sulfate then pressure-filtered. A pale yellow honey product, with an isolated yield of 90% was obtained.

In all the experiments, the components of epoxidized soybean oil and the polyols were separated in a 60–120 mesh silica gel column using a solvent system consisting of toluene and varying proportions of ethyl acetate, for spectroscopic characterization. The molecular mass (MW) was determined by the method of electrospray ionization-mass spectrometry (ESI-MS, WATERS, USA) analysis; the MW of 5-OH polyol, 10-OH polyol and 15-OH polyol were 1056, 1068 and 1439, respectively.

Methods

FTIR spectra (IR Prestige-21, Shimadzu, Japan) of the prepared soybean polyols based on the oxirane cleavage by methanol, sulfuric acid and diethanolamine showed that in comparison with the spectrum of ESO, the disappearance of epoxy groups at 825, 843 cm^{-1} , the emergence of hydroxyl group at 3452 cm^{-1} , and the presence of characteristically secondary hydroxyl groups at 1098 cm^{-1} can be observed in these polyols. Otherwise, the flex vibration of the C–N single bond at 1625 cm^{-1} in 15-OH polyol differed distinctly from 10-OH polyol. These data illustrated the synthesis of polyols were feasible.

$^1\text{H-NMR}$ spectra (Varian 400 spectrometer, USA) of the polyols and the ESO samples reveal information regarding different functional groups. The epoxy protons presents in ESO normally at 3.1 ppm is largely replaced with secondary hydroxyl group and completely disappeared in polyols.

Characterization of thermoproperties

Melting points were obtained with a Netzsch DSC 200-PC differential scanning calorimeter (DSC) operating in N_2 atmosphere (20 mL min^{-1}). The DSC instrument was calibrated with an indium standard and Al was used as reference material. A sample of about 10 mg was scanned at a heating rate of $10^\circ\text{C min}^{-1}$.

The thermostability was tested by thermogravimetry (TG) and derivative thermogravimetry (DTG) with a Netzsch STA 409 PC/PG ana-

lyzer instrument in a dynamic N_2 atmosphere (30 mL min^{-1}). About 12–14 mg of sample was placed in a platinum cell which was transferred to the detector plate, and the furnace was then heated at four heating rates ($5, 10, 15$ and $20^\circ\text{C min}^{-1}$).

The raw data were converted to ASCII files and kinetic analysis was carried out using an in-house program and a Netzsch thermokinetic Program (Version 4.8.1) in the calculation procedure. The corresponding kinetic parameters were computed by nonlinear regression which was the iterative calculation of the minimum sum of least squares, LSQ. For the solution of the system of differential equations, a 5th-degree Runge–Kutta method (Prince–Dormand algorithm) was employed as a subprogram tied into a hybrid regularized Gauss–Newton method.

Results and discussion

Melting points of polyols

Physical properties of the polyols were related to the structural order and the physical state of the polyols above or below the melting point [12].

DSC curves of the prepared soy polyols differed significantly from one another and the starting material ESO (Fig. 1). All polyols displayed at one of the highest melting peaks above 3.4°C ; the values are listed in Table 1. Multiple peaks in these polyols and ESO were ascribed to different crystalline polymorphs that were present in soybean oil [13]. ESO displayed a double peak at -11.3 and -5.3°C . The 5-OH polyol and 10-OH polyol were still liquid at room temperature. 5-OH polyol had one melting peak at 3.4°C and 10-OH polyol two melting peaks at -8.3 and 6.5°C . Hydrogenation caused the shift of the melting points to the higher temperatures to -5.0 and 18.9°C , giving solid grease at room temperature. However, the size of the melting peak was controlled by the crystallization rate and the physical state was largely determined by hydrogen bonding. Increasing the OH content caused an increase in viscosity and an eventual transition from liquid to grease state. The highest melting had the following order in the polyols: 5-OH polyol < 10-OH polyol < 15-OH polyol, due to the content of hydrogen groups in the polyols being in the same order. In a comparison of the melting peaks of polyols from 5-OH polyol to 10-OH polyol, the shape of melting peak was more and more smooth and widened. It illustrated that the introduction of more functional hydroxyl groups into the soybean oil by the oxirane cleavage reaction with CH_3OH , H_2O and $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$ caused a shift and deformation of the melting peak. Hydroxyl groups were introduced in this chemosynthesis reac-

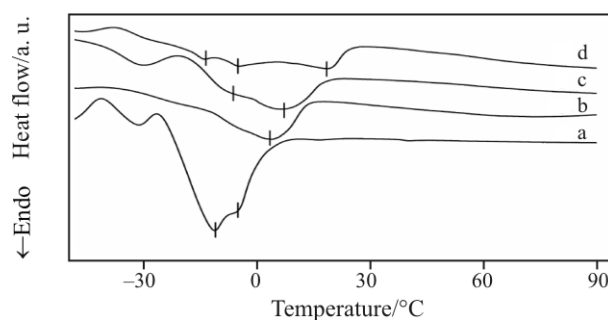


Fig. 1 DSC curves of soy based polyols; a – ESO; b – 5-OH polyol; c – 10-OH polyol; d – 15-OH polyol

Table 1 Melting point of ESO and polyols

Peak	$T/^\circ\text{C}$			
	ESO	5-OH	10-OH	15-OH
1	-11.3	3.4	-8.3	-14.3
2	-5.3	–	6.5	-5.0
3	–	–	–	18.9

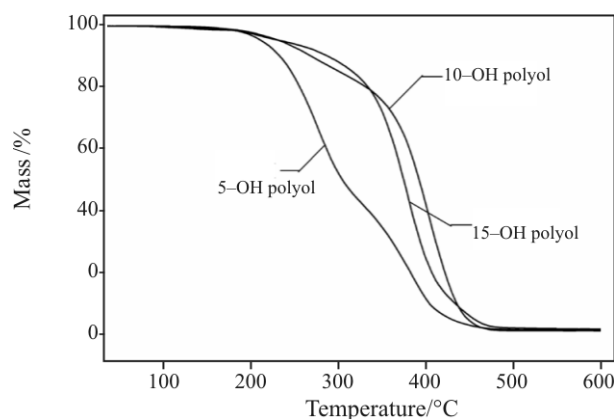


Fig. 2 TG profiles of polyols at $10^\circ\text{C min}^{-1}$ under nitrogen atmosphere

tion and eventually resulted in different number-average functionality of hydroxyl in the resultant polyol [12].

Thermostability of polyols

The TG profile of thermal decomposition progresses for three polyols is shown in Fig. 2 and the more detailed and more exact thermal decomposition progresses, DTG curves, are shown in Fig. 3. A summary of the TG results for the three polyols under nitrogen atmosphere is showed in Table 2. It could be seen that the stabilities are similar to each other under nitrogen atmosphere. However, the more hydroxyl in the formal polyols, the higher the stability is. This could also be explained by the higher hydroxyl equivalents of the polyols.

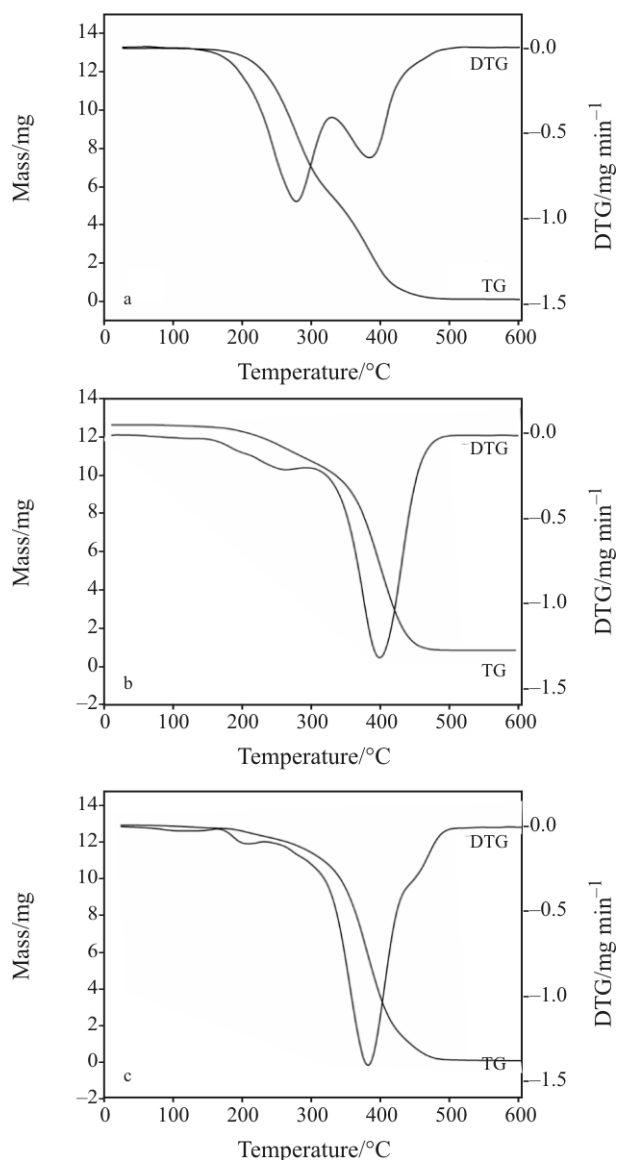


Fig. 3 TG and DTG curves obtained using a heating rate of $10^{\circ}\text{C min}^{-1}$ under dynamic nitrogen atmosphere with a flow rate of 30 mL min^{-1} ; a – 5-OH polyol, b – 10-OH polyol, c – 15-OH polyol

TG curves corresponding to the three studied compounds exhibit some common characteristics and the data are shown in Table 2:

- An insignificant mass loss below 150°C due to the humidity or the reaction reagent from the chemosynthesis of these polyols which is unimportant for our further discussion.
- The first mass loss step corresponds to the loss of water from hydroxyl groups and part fatty carbon chains for formal 5-OH polyol and 10-OH polyol and only water from hydroxyl for the 15-OH polyol.
- The second mass loss step corresponds to the loss of fatty carbon chains with three-membered ring for 5-OH polyol and 10-OH polyol and corresponding to the loss of fatty carbon chains with more stability six-membered ring.
- The 15-OH polyol has the third mass loss step which corresponds to the loss of higher decomposition temperature of nitrile and the other ones have not this mass loss step.

At the beginning of the polyol decomposition, slight mass loss was noticed (Fig. 3), which could be the result of the remains of the reagent adsorbed from the chemosynthesis of these polyols.

As can be seen from TG curve and more precisely from DTG curve of 5-OH polyol (Fig. 3a), the extrapolated onset temperature is 233.4°C and also presenting a less sharp DTG peak at 380°C in the second mass loss step from 324 to 512°C , due to the burnout of the residual carbonaceous material of the previous step.

The 10-OH polyol presents a different behavior during its first thermal decomposition step, which occurs from 150 to 316°C . The lower extrapolated onset temperature is 218.4°C and a distinctly lower DTG peak occurs at 265°C contrasting with the same decomposition step of the 5-OH polyol, because of its molecular structure in the polyol. However, the second decomposition mass loss step present a more homogeneous mass loss DTG peak than the other

Table 2 TG results for three polyols under nitrogen atmosphere when $\beta=10^{\circ}\text{C min}^{-1}$

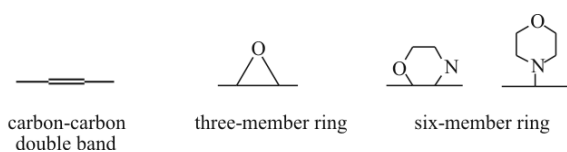
Project	5-OH polyol	10-OH polyol	15-OH polyol
Onset $T/^{\circ}\text{C}$	233.4	218.4	186.8
Primary region $T/^{\circ}\text{C}$	160–324	150–316	163–233
Primary mass loss/%	45.45	16.72	3.56
Secondary region $T/^{\circ}\text{C}$	324–512	316–509	233–425
Secondary mass loss/%	41.83	82.24	83.59
Tertiary region $T/^{\circ}\text{C}$	–	–	425–512
Tertiary mass loss/%	–	–	10.37
Residue at $600^{\circ}\text{C}/\%$	0.56	0.39	0.94

polyols, as can be seen in the DTG curve (Fig. 3b). Its similar behavior to the other ones occurs because of the combustion of the carbonaceous residue.

The thermal decomposition of 15-OH polyol displays a different mass loss course showing three mass loss steps (Fig. 3c). The extrapolated onset temperature is 186.8°C and a sharpest DTG peak can be noticed at 378°C. The additional mass loss step occurs from 425 to 512°C and also presents a blurry DTG peak about 455°C. It is due to the introduction of nitrogen element into the 15-OH polyol caused the polyol has the function of higher thermal resistance. As a result the nitride from the second mass loss step decomposes in the last mass loss step.

It can be concluded that the onset temperature of the formal polyols decreases in the following order: 5-OH polyol > 10-OH polyol > 15-OH polyol in the first mass loss region.

The higher the onset temperature of decomposition of the polyol, the higher its thermal stability is. This property is of significant practical importance, especially when the polyols react with TDI, MDI, HDI and other type of diisocyanate to manufacture any useful polyurethane elastomer, in order to avoid the rupture of glyceryl chain of these formal polyols due to drastic exothermic reactions. The decomposition of the 5-OH polyol hydroxyl into water is difficult, but 10-OH polyols easier forms water from hydroxyl. 15-OH polyols are the most easily translated hydroxyl into water. It appears that the higher amounts of hydroxyl in the polyols can increase the thermal stability of these polyols and shift the process of mass loss toward higher temperatures. The hydroxyl in the 5-OH polyol can translate into carbon double bond (C=C) and 10-OH polyol can translate into a less stable three-membered ring (Scheme 2). The probability of the hydroxyl in the 10-OH polyol translating into a three-member ring is larger than for the 5-OH polyol once it has twice the number of hydroxyl. In the 15-OH polyol, the adjacent hydroxyl can easily translate into two different forms of more stable six-member rings (Scheme 2) during the first mass loss step. Consequently, the mass loss measured by TG shifted to somewhat higher temperatures in the secondary region of mass loss for these polyols. Taking the stability and probability of the ring being changed from the hydroxyl in different polyols into



Scheme 2 Part structure of the fatty acid carbon chains during degradation

account, the thermal stability decreases in the following order: 15-OH polyol > 10-OH polyol > 5-OH polyol in the first mass loss steps.

Kinetic analysis of polyols

The kinetic study should be run above 150°C to ensure total vaporization of water from the atmosphere or reactants.

The kinetic decomposition of the polyols was analyzed with a non-isothermal technique. Friedman developed a differential isoconversional method whereby the activation energy for a mass loss process could be determined using Eq. (3) for the three formal polyols [14, 15]:

$$\lg\left(\frac{\beta d\alpha}{dT}\right) = \lg[AF(\alpha)] - \frac{E}{2.303RT} \quad (1)$$

and

$$\frac{dx}{dt} = \frac{\beta d\alpha}{dT} \quad (2)$$

then

$$\lg\left(\frac{dx}{dt}\right) = \lg[AF(\alpha)] - \frac{E}{2.303RT} \quad (3)$$

where β is the heating rate, T is the temperature, t is the time, R is the gas constant, α is the conversion degree, A is the pre-exponential factor and E is the activation energy in sense of Arrhenius equation. The slope of the straight line obtained by plotting $\lg(dx/dt)$ vs. $1/T$ at any level of same conversion degree can be used to calculate the activation energy for the mass loss process of formal polyols under nitrogen atmosphere. A typical $\lg(dx/dt)$ vs. $1/T$ plot calculated for the three formal polyols under nitrogen atmosphere is shown in Fig. 4.

The activation energy (E) of the polyol sample by the Friedman's analyses during the thermal degradation under nitrogen atmosphere is shown as Fig. 5. As can be seen from the thermal decomposition of 5-OH polyol, the activation energy is the lowest according to the appointed conversion degree in the three polyols. It shows that the 5-OH polyol has the lowest stability during thermal decomposition. A turning point is found to be at 332.2°C which is due to the three-member ring begins to rupture according to the 60% mass loss and then an approximate energy flat is come to appear with the reposeful decomposition.

The activation energy of 10-OH polyol slowly increases and ends at 316°C relating to 17.37% mass loss. The water from intramolecular reaction of adjacent hydroxyl of the 10-OH polyol disappears and part fatty carbon chains partly rupture in the first mass loss step. The activation energy is 165 kJ mol⁻¹ is related

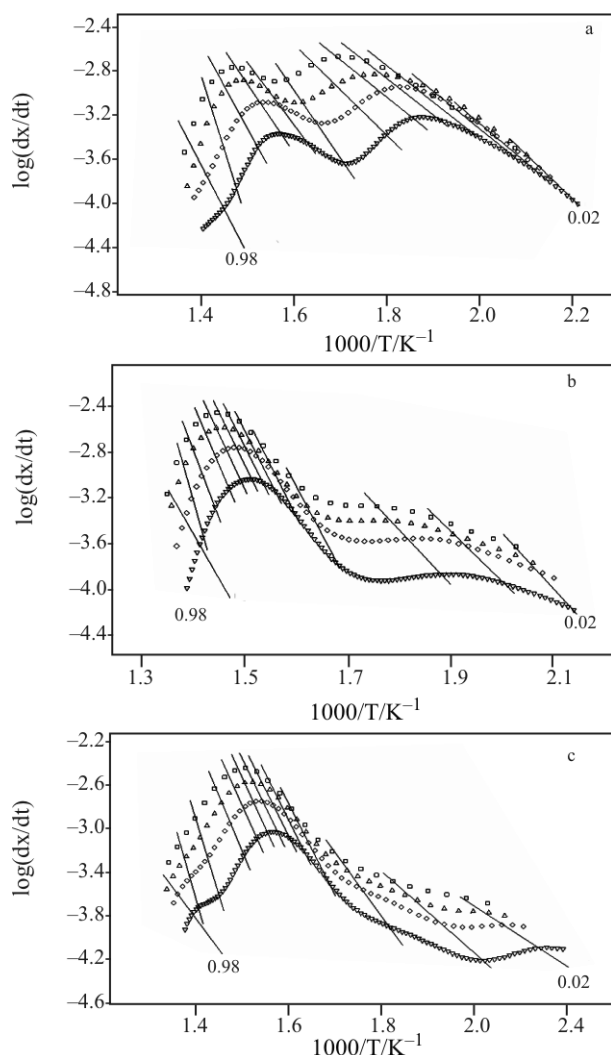


Fig. 4 Friedman's analyses of: a – 5-OH polyol; b – 10-OH polyol; c – 15-OH polyol

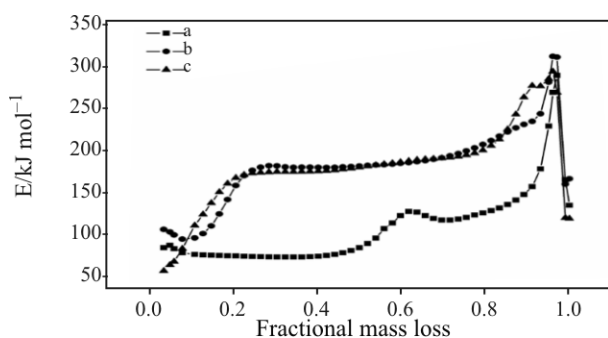


Fig. 5 Activation energy plotted from Friedman's analyses: a – 5-OH polyol; b – 10-OH polyol; c – 15-OH polyol

to 19 mass% loss and is the beginning of three-member ring rupture. There is an energy plateau at the temperature of 509°C till the three-member ring from the adjacent hydroxyl and fatty carbon chains decompose completely in the secondary mass loss.

The activation energy of degradation process of 15-OH polyol is similar to the 10-OH polyol, but the mass loss due to the disappearance of water from intramolecular reaction of adjacent hydroxyl is slightly prior to arrive because the six-member ring is more stable than three-member ring from 10-OH polyol. There is also a lesser turning point due to the appearance of the higher decomposition temperature of nitride.

Conclusions

- Higher number-average functionality of hydroxyl in polyols cause the melting peaks to shift to higher temperatures and the shape of melting peaks to become smoother and wider, due to oligomerization.
- The thermal stability in an increasing order is: 5-OH polyol < 10-OH polyol < 15-OH polyol in the first mass loss steps because the extrapolated onset temperature of the polyols had the same order.
- The 5-OH polyol and 10-OH polyol had two mass loss steps but 15-OH polyol has an additional mass loss step because of the appearance of nitride at the higher decomposition temperature from the second mass loss step.
- The 15-OH polyol was prior to arrive at the mass loss region contrasted with the other samples because it had the highest stability and probability of the ring changed from the adjacent hydroxyl in the glyceride molecule.

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