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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 PAEZ

Asunto: Radicación: 14-23080- -1
 Trámite: 2
 Evento: 1
 Actuación: 519
 Oficio: 4793
 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° 14-023080-00000-0000	4/Febrero/2014
Reivindicaciones:	Rad. N° 14-023080-00000-0000	4/Febrero/2014
Dibujos:	Rad. N° 14-023080-00000-0000	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 17.

Título de la solicitud: “Proceso de obtención de poliuretanos a partir de aceite de palma y poliuretanos obtenidos” (Ver. Pág. 4 del Rad. N° 14-023080-00000-0000).

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)

La reivindicación 2 no es clara porque el peso molecular del poliol es un resultado a alcanzar, lo que no está permitido, no define al 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 remplazarla por las características esenciales estructurales que contribuyen a la obtención de ese efecto.

La reivindicación 15 no es clara porque presenta una falsa dependencia a la reivindicación 1 al ser la reivindicación 15 una reivindicación de producto mientras la reivindicación 1 una reivindicación de método. Se sugiere definir el producto por sus características esenciales estructurales.

Las reivindicaciones 16 y 17 no son claras porque las expresiones “densidad”, “módulo de Young” y “esfuerzo máximo” son parámetros del poliuretano obtenido y no deberían caracterizar el compuesto solamente por sus parámetros, si es posible definirlo de otra manera. Se sugiere definirlo por sus características esenciales estructurales.

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.

Item	Documento	Título	Fecha de Publicación
D1	Art 1 ¹	“Water-borne and air-drying oil-based resins”	2004
D2	Art 2 ²	“Processing and Properties of Palm Oil-Based Rigid Polyurethane Foam”	2007
D3	EP 1006133	“Polyurethane foam, process for producing the same, and foam forming composition”	21/Noviembre/2007

¹ Gündüz, et al. Progress in organic coatings. 2004. Vol. 49. Págs. 259 a 269.

² Chuayjuljit et al. Journal of Metals, Materials and Minerals.2007. Vol 17 (1). Págs. 17 a 23.

³ <http://www.freepatentsonline.com/EP1006133B1.html>

El documento D1 divulga un método para la maleinización de triglicéridos y su posterior uso para la formación de barniz de poliuretano (Pág. 260, Col. 2, Párr. 2 y Párr. 3, Pág. 261, Tabla 1, Pág. 261, Col. 2, Párr. 5 a Pág. 262, Párr. 5).

El documento D2 divulga polioles a partir de aceite de palma adecuados para realizar espumas rígidas (Pág. 19, Col. 1, Párr. 5, Pág. 23, Col. 1, Párr.2).

El documento D3³ divulga espumas de poliuretano con densidades de 0,100 a 1,800 g/cm₃ y de 0,015 a 0,200 g/cm³ (Pág. 12, Párr. 89, Pág. 11, Párr. 77 y Párr. 79).

6. Examen de Patentabilidad (Art 14 D486)

Novedad (Art 16 D486)

La reivindicación 15 consiste en “*Poliuretano CARACTERIZADO PORQUE se obtiene por el proceso de la reivindicación 1*” (Ver Pág. 48 del Rad. N° 14-023080-00000-0000).

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

Características esenciales	D3
Poliuretano caracterizado porque se obtiene por el proceso de la reivindicación 1	La densidad del poliuretano esta entre 0,100 y 1,800 g/cm ³ o entre 0,015 y 0,200 g/cm ³ (Pág. 11, Párr. 77 y Párr. 79, Pág. 12, Párr. 89).

De acuerdo con la tabla anterior, las características esenciales del poliuretano de la reivindicación 15 habían sido divulgadas previamente en el documento D3, por lo tanto, la materia reivindicada no es nueva.

Adicionalmente se reitera que, las reivindicaciones 16 y 17 no mencionan características técnicas y/o características tangibles adicionales que puedan brindarle novedad al objeto de la reivindicación 15, puesto que se encuentran redactadas en términos de parámetros. En este caso llama la atención que con un mismo procedimiento se obtengan dos espumas de características diferentes.

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 Pág. 46 del Rad. N° 14-023080-00000-0000).

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	No se menciona	Proceso para la obtención de poliuretanos a partir de aceite de palma (Pág. 18, Col. 2).
a) Mezclar, calentar y agitar aceite de palma con hidróxido de sodio y una solución etanol-agua 1.1	Se mezcla aceite de girasol con hidróxido de sodio y una solución etanol-agua 1:1 (Pág. 260, Col. 2, Párr. 5).	No se menciona
b) Adicionar ácido sulfúrico concentrado a la mezcla del paso a) hasta que se observe la separación de las fases	Se reacciona el jabón obtenido con una cantidad estequiométrica de ácido sulfúrico (Pág. 260, Col. 2, Párr. 5 a Pág. 261, Col. 1, Párr. 1).	No se menciona

c) Adicionar solución saturada de cloruro de sodio a la mezcla del paso b)	Se adiciona cloruro de sodio para separar las fases en la saponificación (Pág. 260, Col. 2, Párr. 5).	No se menciona
d) Descartar la fase acuosa obtenida en el paso c), después de la completa separación de fases	Se separa la fase orgánica de la fase acuosa y la fase orgánica se concentra por filtración descartando la fase acuosa (Pág. 261, Col. 1, Párr. 1).	No se menciona
e) Lavar con agua a una temperatura entre 70°C y 80°C la fase orgánica restante del paso d)	Se lava con agua la fase orgánica varias veces (Pág. 261, Col. 1, Párr. 1).	No se menciona
f) Calentar y agitar la fase orgánica del paso e) y someter a evaporación al vacío obteniéndose los ácidos grasos	Se remueve el agua por evaporación al vacío (Pág. 261, Col. 1, Párr. 1). En este punto no se observa efecto importante en el orden de adición del ácido sulfúrico y el cloruro de sodio, pues se obtiene con cualquier orden ácidos grasos purificados.	No se menciona
g) Mezclar los ácidos grasos obtenidos en el paso f) con glicerol previamente bloqueado y un catalizador, calentar y agitar	Se mezclan los ácidos grasos con ácido para toluen sulfónico como catalizador y glicerol bloqueado a 90°C (Pág. 261, Col. 1, Párr. 3).	No se menciona
h) Lavar con agua a una temperatura entre 70°C y 80°C la mezcla del paso g)	Se lava con agua varias veces para remover el catalizador (Pág. 261, Col. 1, Párr. 4).	No se menciona
i) Separar la fase acuosa obtenida en el paso h) y descartarla	Para remover el agua generada en la reacción se emplea tolueno, el cual se separa por destilación retirando así el agua (Pág. 261, Col. 1, Párr. 3).	No se menciona
j) Tratar la fase orgánica restante en el paso i) mediante evaporación al vacío para obtener monoglicérido bloqueado	El tolueno se separa de la fase orgánica por evaporación al vacío, obteniéndose monoglicérido bloqueado purificado (Pág. 261, Col. 1, Párr. 3 y Párr. 4).	No se menciona
k) Adicionar el monoglicérido bloqueado del paso j) anhídrido maléico, calentar y agitar bajo atmósfera de nitrógeno	Se tiene en la reacción monoglicérido bloqueado, anhídrido maléico y se somete a 200°C en atmósfera de nitrógeno y con agitación (Pág. 261, Col. 1, Pág. 260, Col. 2, Párr. 1).	No se menciona
l) Enfriar la mezcla del paso k) hasta 100°C	Se enfría a 100°C para que ocurra la reacción con ácido sulfúrico (Pág. 261, Col. 2, Párr. 3).	No se menciona
m) Adicionar ácido sulfúrico al producto de la reacción del paso l)		No se menciona
n) Lavar con agua a una temperatura entre 70°C y 80°C y decantar el producto de reacción obtenido en el paso separar la fase acuosa obtenida en el paso m)	La decantación es una etapa unitaria usada para separar fases de compuestos hidrofóbicos de los hidrofílicos (Pág. 261, Col. 1, Párr. 1). Aquí Se lava varias veces con agua y se evapora el agua con el metil etil cetona quedando al final el poliol purificado (Pág. 261, Col. 2, Párr. 3).	No se menciona
o) Separar la fase acuosa obtenida en el		No se menciona

paso m)		
p) Lavar la fase orgánica obtenida en el paso m)		No se menciona
q) Evaporar la fase orgánica del paso n) para obtener el poliol		No se menciona
r) Al poliol obtenido del paso q), se le adiciona surfactante y metil etil cetona y hacer reaccionar la mezcla a una temperatura de 50°C durante un periodo de treinta minutos	El poliol se hace reaccionar con MEK (metil etil cetona) y HTPB (hidrox terminal polibutadieno, el cual es un agente un surfactante, propelante) durante 30 minutos a 50°C (Pág. 261. Col. 2. Párr. 6).	No se menciona
s) Adicionar toluen diisocianato con agitación mecánica a una temperatura de 70°C	A 70 °C se adiciona el toluen diisocianato (TDI) y se agita por tres horas (Pág. 262, Col. 1, Párr. 2).	No se menciona
t) Enfriar a 50°C	Se enfria a 50°C y se adiciona metil etil cetoxima MEKO por 2 horas (Pág. 262, Col. 1, Párr. 3).	No se menciona
u) Adicionar metil etil cetoxima hasta bloquear los grupos NCO libres		No se menciona
v) Adicionar trietilamina en un reactor agitado	Se adiciona TEA trietilamina y se agita por 30 min a 50°C (Pág. 262, Col. 1, Párr. 4).	No se menciona
w) Adicionar agua, gota a gota, para formar una emulsión en una cantidad de 50% en peso.	Bajo agitación continua y gota a gota se adiciona agua hasta un 50% en peso (Pág. 262, Col. 1, Párr. 5).	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 obtenidos de aceites vegetales.

La diferencia entre la invención, definida en la reivindicación 1 y el método del documento D1 consiste en que D1 no menciona que la obtención de poliol sea a partir de aceite de palma como materia prima.

La diferencia entre la invención, definida en la reivindicación 1 y el método del documento D2 consiste en que en D2 no se menciona la reacción de maleinización con un monoglicérido bloqueado ni la reacción de polimerización con TDI.

No se evidencia algún efecto técnico que logre la diferencia al obtener un poliol a partir de aceite de palma o de otro aceite renovable porque la solución de la presente solicitud ya esta divulgada en el documento D1 que divulga la obtencion de poliol a partir de aceite de girasol, en donde el proceso posee etapas que conllevan a obtener las mismas características del monoglicerido bloqueado, del poliol y del barniz de poliuretano.

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

Sin embargo, el empleo de aceite de palma como triglicérido para obtener un poliol y su posterior uso para obtener un poliuretano, ya está divulgado en el documento D2 que se refiere a la obtención, a partir de aceite de palma, de polioles adecuados

para realizar espumas rígidas (Pág. 19, Col. 1, Párr. 5, Pág. 23, Col. 1, Párr.2).

En consecuencia, una persona normalmente versada en la materia incluiría el aceite de palma como materia prima para la obtención del polioliol y asimismo incluiría el polioliol de D2 en el procedimiento para la fabricación 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 2: polioliol con peso molecular de 455 g/mol (Pág. 261, Col. 2, Párr. 4).

Reivindicación 3: la temperatura del paso a) a 80°C durante el tiempo necesario para homogenización (Pág. 260, Col. 2, Párr. 5).

Reivindicación 6: el glicerol bloqueado viene de a) mezclar glicerol, MEK, ácido toluen sulfónico como catalizador y tolueno; b) calentar la mezcla anterior a 90°C (Pág. 261, Col. 1, Párr. 3).

Reivindicación 10: la reacción de monoglicérido bloqueado con anhídrido maléico se somete a 200°C en atmosfera de nitrógeno y con agitación (Pág. 261, Col. 1, Pág. 260, Col. 2, Párr. 1).

Reivindicación 11: se disminuye la temperatura hasta 100°C antes de la adición del ácido sulfúrico, en donde la agitación durante las reacciones es requerida (Pág. 261, Col. 2, Párr. 3, Pág. 261, Col. 1, Pág. 260, Col. 2, Párr. 1).

Asimismo, el documento D2 divulga las características de las reivindicaciones dependientes así:

Reivindicación 2: polioliol con número de hidroxilo de 385 mg KOH/g (Pág. 19, Col. 1, Párr. 5).

Por otra parte la reivindicaciones 4, 5, 7 a 9 y 11 a 14 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”*⁴, el cual conoce que:

Reivindicación 4: lavados hasta pH neutro de los productos obtenidos de la transformación de aceites y/o ácidos grasos⁵.

Reivindicación 5: la estabilidad de los aceites que contienen ácidos grasos con respecto a la temperatura⁶, por lo que calentar para evaporar como lo realiza la solicitud y evaporar al vacío como se menciona en D1 no produce un efecto técnico inesperado.

Reivindicación 7: la estabilidad de los aceites que contienen ácidos grasos con respecto a la temperatura⁶, por lo que calentar para evaporar durante un tiempo especificado como lo realiza la solicitud y evaporar al vacío como se menciona en D1 no produce un efecto técnico inesperado.

⁴ Proceso 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.

⁵ Sinadinovic-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.

⁶ Souza et al. A thremoanalytic and kinetic study of sunflower oil. Brazilian Journal of Chemical Engineering. Vol. 21(2).2000. Pág. 268, Pág. 269, Figs 2 y 3.

Reivindicación 8: lavados hasta pH neutro de los productos obtenidos de la transformación de aceites y/o ácidos grasos⁵.

Reivindicación 9: la estabilidad de los aceites que contienen ácidos grasos con respecto a la temperatura⁶, por lo que calentar para evaporar durante un tiempo especificado como lo realiza la solicitud y evaporar al vacío como se menciona en D1 no produce un efecto técnico inesperado.

Reivindicación 12: la estabilidad de los polioles obtenidos a partir de aceites naturales con respecto a la temperatura⁷, por lo que lavar con agua caliente durante un tiempo especificado como lo realiza la solicitud no produce un efecto técnico inesperado.

Reivindicación 13: la estabilidad de los polioles obtenidos a partir de aceites naturales con respecto a la temperatura⁷, por lo que calentar para evaporar durante un tiempo especificado como lo realiza la solicitud y evaporar al vacío como se menciona en D1 no produce un efecto técnico inesperado.

Reivindicación 14: NaOH como catalizador de glicerólisis⁸.

Puesto que las reivindicaciones dependientes 2 a 14 no mencionan características adicionales que hagan inventiva la solicitud, se considera que tales reivindicaciones tampoco tienen nivel inventivo.

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 14	Nivel inventivo
D2	Art 2	1 a 14	Nivel inventivo
D3	EP 1006133	15 a 17	Novedad

⁷ Yang, et al. Thermal analysis of soybean oil based polyols. Journal of Thermal Analysis and Calorimetry. 2009. Vol. 95 (3). (Pág. 980, Fig. 3).

⁸Tanaka, et al. Bioresource technology. 2008. Vol. 99. Págs. 3811, Párr.2.

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.



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El anterior requerimiento fue notificado por fijación en lista, de fecha 2014-04-29

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Water-borne and air-drying oil-based resins

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Abstract

New water-borne polyurethane resins were produced using maleinized monoglyceride (MMG), hydroxyl-terminated polybutadiene (HTPB), toluene di-isocyanate, and ethylene diamine (EDA). Maleinization was performed in order to insert hydrophilic groups in the fatty acid residues, which were then inserted to the backbone of polyurethane. The MMG was mixed with HTPB in different proportions, and the mixture was used as the polyol part of water-borne polyurethane resin. It was then reacted with toluene di-isocyanate, and the isocyanate end groups were blocked with methyl ethyl ketoxime (MEKO). The ratio of MMG to total polyol was changed between 40 and 70 mol%, while the [NCO]/[OH] ratio was kept at 1.5 in all samples. The carboxylic acid groups of MMG were then neutralized with triethyl amine. The formation of ionic groups imparts water dispersibility. Chain extension was performed by adding EDA and baking at 125 °C. Hardness, adhesion, impact resistance, bending, and abrasion resistance tests were applied to the specimens. The samples exhibited good physical and mechanical properties.

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Keywords: Water-borne; Water dispersed; Polyurethane; Maleinization; Monoglyceride; Air-drying

1. Introduction

Polyurethanes exhibit excellent abrasion resistance, toughness, chemical and corrosion resistance and a wide range of mechanical strengths, thus they have found extensive applications in the high performance coatings for the automotive, appliance, and wood industries [1]. In the 1980s, the automakers started to shift from solvent-based to water-based paints to reduce the amount of volatile combustibles. The increasing trend towards water-dispersed paints accelerated the research on the development of new type of polymeric resins for use in paint industry [2,3]. The research on water-borne paints goes down to early fifties, and the work was mostly concentrated on the use of maleinized oils [4].

Most polyurethane paints available in the market are usually made by using polyester polyols to impart sufficient rigidity to the resin. However, polyether polyols are also used as partial substitute to make resins with improved flexibility. Polyethers increase also the dispersion of the resin in water because they have higher number of hydrophilic groups on

the backbone. The use of polyethylene and polybutylene glycol at appropriate ratios may help to balance the hydrophilic and hydrophobic properties at the desired level. Water-borne alkyds drew continuous attention as the availability of raw materials and the superior properties of the product are concerned. The alkyd resins may also be made water dispersible by mixing a normally synthesized resin with a specially synthesized alkyd which contains high acidic groups. The high acidic groups can be achieved by using a chemical with high functionality such as trimellitic anhydride. The styrenated alkyd may be made water-borne by using hydrophilic monomers such as acrylic acid or methacrylic acid [4]. The research on oil containing water-borne resins is still an active subject in paint industry and new patents were introduced using different raw materials and techniques [5–8]. In recent years, water-dispersed epoxy resins also have gained importance [9]. Although water-dispersed paints display excellent performance in many areas of applications they lack abrasion resistance, chemical resistance and general durability [10]. The research work on water-borne resins and paints cover a wide range from synthesis to characterization [11–15].

Water dispersion of polyurethanes is usually achieved by having carboxyl acid residues on the backbone and quaternizing these groups by tertiary amines. The organic salts thus formed become dispersible in water. The most preferred

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monomer to incorporate hydrophilic group is dimethylol propionic acid though tartaric acid can also be used with some precaution; that is, heavy branching must be prevented during synthesis when tartaric acid is used [14,15]. Polyurethanes contain a soft and a hard segment on the backbone with polyesters (or polyethers) comprising the soft segment, and the urethane group the hard segmental part. Air-drying polyurethane resins can be synthesized by substituting the polyester with monomers containing double bonds on the backbone such as monoglycerides [15]. However, the use of pure monoglyceride results in a thick mixture which is apt to easy gelation. Therefore, it needs to be diluted by using a polyol. The polyol can be of polyester or polyether origin.

The aim of this work was to synthesize water dispersible polyurethane resin containing (i) fatty acid residues to provide air drying and (ii) maleinized fatty acid residues to achieve water dispersion. In other words, the traditionally used dimethylol propionic acid has been substituted by maleinized fatty acids. To improve air drying hydroxyl-terminated polybutadiene (HTPB) was partly used on the backbone. The research work concentrated on synthesizing a maleinized monoglyceride (MMG) derivative from sunflower oil. The monoglyceride derivative contained both fatty acid residues and hydrophilic groups. Two different MMG derivatives were synthesized and the resins made from them were characterized for their properties.

2. Experimental

2.1. Raw materials

The raw materials used were sunflower oil, sodium hydroxide (Merck), sulfuric acid (99.5% pure; Merck), methyl ethyl ketone (99.5% pure; Delta Kimya), toluene sulfonic acid, glycerine (99.5% pure; Birpa Ltd. Ş.), maleic anhydride (Volkan Boya), HTPB (MW = 2700 g/mol; SAGE), toluene diisocyanate (TDI) an isomeric commercial grade mixture (İşbir A.Ş.), methyl ethyl ketoxime (MEKO; Volkan Boya), triethylamine (TEA; ÇBS A.Ş.), ethylene diamine (EDA; Merck), and nitrogen gas (99.999% pure; Habaş).

HTPB was dehydrated by passing nitrogen gas through it for 30 h. MEK and MEKO were dehydrated over molecular sieves. MMG, after its production, was dehydrated under vacuum at 50 °C, for about 2 h, and then magnesium sulfate salt was used to remove any remaining water. Other materials were used as-received.

2.2. Synthesis of MMG derivatives

MMG derivative was produced by two different methods. They are denoted here as Method I and Method II. A number of trials were made to synthesize MMG by direct maleinization of monoglyceride. However, gelation took place in all of these trials because of the reaction of anhydride groups

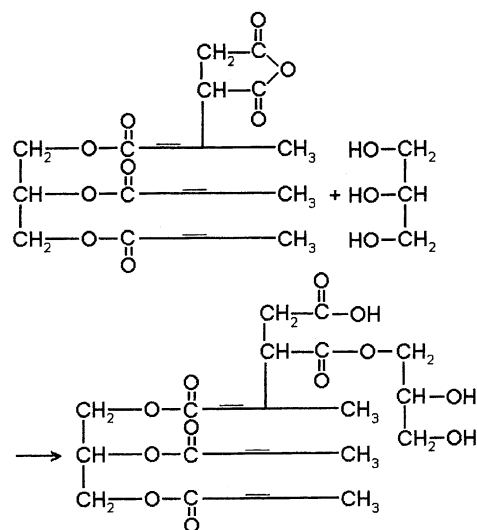
of maleic anhydride and hydroxyl groups of glycerin. In another trial, the oil was maleinized and then reacted with glycerin, but the material gelled in this case too. Therefore, two different methods described below were used to synthesize MMG derivative. The experiments were carried in a 5-necked glass reactor of about 1 l in volume. It is equipped with a stirrer, condenser, thermometer, nitrogen and feed inlet.

2.2.1. Method I

The following steps were performed:

1. The sunflower oil was reacted with maleic anhydride at 200 °C under nitrogen atmosphere for 3 h.
2. The maleinized oil was cooled to 100 °C, and glycerine was added to the reactor. The reaction continued until the acid number came down to a value of 90. As seen in equation the maleinized oil was hydrolyzed with glycerin to yield monoglyceride. It now has two hydroxyl groups to react with a di-isocyanate to make polyurethane, has one carboxylic group that can be used for water dispersion, and two fatty acid residues having double bonds for air drying.

However, this MMG derivative, named MMG-I, resulted in brownish color when used in making polyurethane resin. Therefore, another MMG derivative was synthesized by following another method:



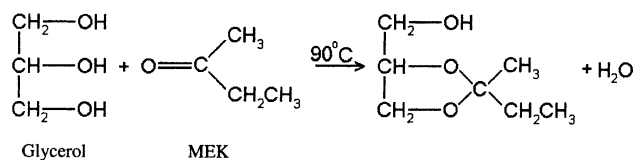
2.2.2. Method II

In this method we needed to use fatty acids in the synthesis of MMG. Therefore, fatty acids were first obtained from the alcoholysis of sunflower oil. The oil was mixed with 1:1 ethanol–water solution, and stoichiometric amount of sodium hydroxide (3 mol per mole of oil) was added. The hydrolysis reaction was carried at 80 °C under reflux until a homogeneous mixture was obtained. The mixture was poured into a saturated solution of sodium chloride in order to precipitate the soap. Then soap was dissolved in water and

reacted with stoichiometric quantity of sulfuric acid. This separates fatty acid phase from water phase. The saturated fatty acids, stearic acid (6 wt.%) and palmitic acid (11 wt.%) with melting points of 69.6 and 63.1 °C, respectively, precipitate at room temperature, and they were filtered out to increase the unsaturation in the final product. The liquid fatty acid phase was washed with water for several times and put under vacuum to remove water.

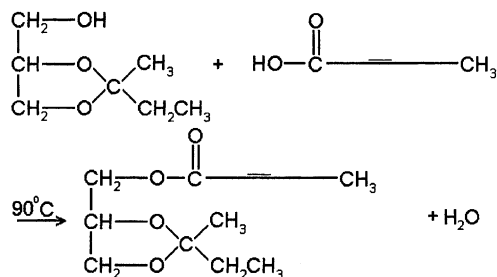
In order to synthesize MMG the following steps were performed:

1. Glycerol was reacted with MEK at 90 °C, using toluene sulfonic acid as a catalyst. Thus two of the hydroxyl groups of glycerine were blocked with MEK:



The reaction water was removed by azeotropic distillation with toluene during reaction.

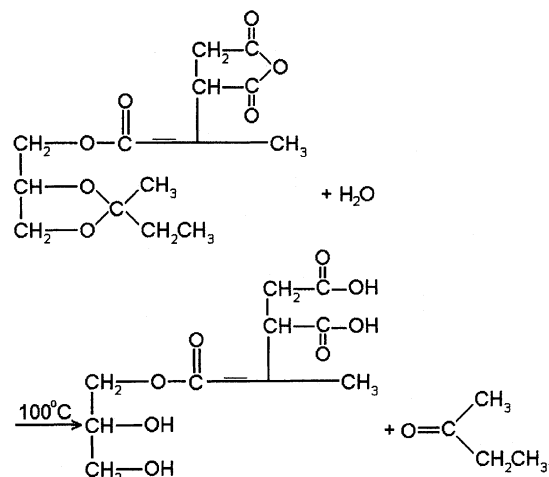
2. The resultant material was reacted with fatty acid mixture using the same catalyst. The fatty acid mixture contains about 35% by weight oleic acid, 62.6% linoleic, and 2.4% linolenic acid. Thus totally unsaturated fatty acid residues are introduced into the structure:



The resulting water was again removed by azeotropic distillation with toluene.

3. The material was washed with water for several times to remove the catalyst. Then, toluene was removed under vacuum.

4. The synthesized chemical was maleinized by reacting it with 30 mol% of maleic anhydride at 200 °C and under nitrogen atmosphere.
5. The maleinized product was hydrolyzed by reacting it with water in the presence of several drops of sulfuric acid, and thus a new maleinized monoglyceride derivative, named MMG-II, was obtained.
6. The MMG derivative was washed with water for several times and then put under vacuum for about 3 h to remove water and MEK produced as a by product:



As the two MMGs are compared, both have two hydroxyl groups, MMG-I has one carboxyl group while MMG-II has two. MMG-I has an additional two more fatty acid residues. The molecular weight of MMG-I is 1053 g/mol, and that of MMG-II is 455 g/mol.

2.3. Water-dispersed polyurethane varnish production

In all experiments, the [NCO]/[OH] ratio was kept at 1.5 in order to assure NCO termination of the prepolymer. The experiments were repeated by changing the ratio of MMG to HTPB. Several formulations of the feed are given in Table 1. The following procedure was carried out in making water-dispersed polyurethane:

1. HTPB and MMG were dissolved in MEK by stirring the mixture for 30 min at 50 °C. This was done in

Table 1
Basic formulations of the resin

Method	Sample	Ratio ^a (%)	MMG (mol)	HTPB (mol)	TDI (mol)	MEKO (mol)	TEA (mol)	EDA (mol)
I	A1	40	0.8	1.2	3.0	2.0	0.8	1.0
I	A2	50	1.0	1.0	3.0	2.0	1.0	1.0
I	A3	60	1.2	0.8	3.0	2.0	1.2	1.0
I	A4	70	1.4	0.6	3.0	2.0	1.4	1.0
II	B1	50	1.0	1.0	3.0	2.0	0.6	1.0
II	B2	55	1.1	0.9	3.0	2.0	0.66	1.0
II	B3	60	1.2	0.8	3.0	2.0	0.72	1.0
II	B4	65	1.3	0.7	3.0	2.0	0.78	1.0
II	B5	70	1.4	0.6	3.0	2.0	0.84	1.0

^a MMG/(MMG + HTPB).

order to have a homogeneous distribution of hydrophilic molecules in the polymer backbone.

2. TDI was added to the mixture and the reaction continued for 3 h with stirring at 70 °C. The reaction time was determined by using di-butylamine back titration method.
3. After the completion of the reaction, the prepolymer was cooled to 50 °C, and the free NCO groups of the prepolymer were blocked with MEKO for approximately 2 h. This step is not necessary. However, it is done to improve the shelf-life of the resin.
4. TEA was added to the solution to neutralize the carboxylic groups, and the mixture was stirred for 30 min, while maintaining the temperature at 50 °C.
5. Water was added to the solution at an amount to make 50% of the total mass from a stop-cock burette by one drop per two or three seconds under continuous stirring.

3. Results and discussion

3.1. Chain extension by baking

Ethylene diamine was used for the chain extension of blocked isocyanate groups. It was added at stoichiometric amounts to all samples prepared. It was added 2–3 h before the application step because it causes gelation at room temperature in 4 days after its addition.

3.2. Preparation of test panels

A standard of 30 μm wet film thickness was applied to test panels. This was done by using film casting knife (Braive-Instruments) on the panels. After casting, the test panels were put in an oven, where the temperature was increased to 125 °C, and maintained at this temperature for 3 h. The varnishes which were produced using MMG produced through Method II required a temperature of 175 °C to form a non-tacky film. The films dried in 1 day at room temperature without using any drier.

3.3. NMR spectroscopy

A Bruker-Spectrospin Avance (DPX 400) Ultra-Shield Nuclear Magnetic Resonance instrument was used to characterize the MMG. The characterization by using ^1H NMR spectroscopy was done only for MMG-II because the process used is a novel one. The characterization was done by comparing the spectroscopy of a mixture of maleic anhydride and monoglyceride in Fig. 1 with that of MMG in Fig. 2.

The results showed that the double bonds of MMG disappeared after the reaction. In Fig. 1, the peak at 6.2 ppm denotes the double bonds of maleic anhydride, and it disappeared after the reaction of maleic anhydride with monoglyceride as shown in Fig. 2. The other peaks appear in both figures because they have similar structure. The peak

at 5.2 ppm denotes the hydrogen atom bonded to the secondary carbon atom in the monoglyceride molecule. This peak covers also carbon–carbon double bond of the fatty acid residue. The peak at 4.1 ppm denotes the carboxylic and ester groups. The peak at 2.6 ppm corresponds to $-\text{CH}_2-$ groups adjacent to double bond in the fatty acid residue, and the one at 2.25 ppm denotes the $-\text{CH}_2-$ groups adjacent to the ester bond and the groups that are not bonded to the carbon atoms in the double bonds. The peak at 2.0 ppm corresponds to the $-\text{CH}_2-$ from maleic anhydride, and the one at 1.3 ppm denotes the $-\text{CH}_2-$ groups adjacent to methyl groups in the fatty acids and methyl ethyl ketone. The peak at 0.9 ppm denotes the $-\text{CH}_3$ group in the fatty acid and methyl ethyl ketone.

3.4. IR spectra

Hitachi (Model: 270-30) Infrared Spectrophotometer was used to characterize the samples. The IR spectrum of MMG-I and of MMG-II are shown in Figs. 3 and 4, respectively.

The peak at 3500 cm^{-1} corresponds to OH stretching, the small shoulder at 3000 cm^{-1} corresponds to unsaturated CH stretching, and the peak at 2900 cm^{-1} corresponds to CH_2 stretching. The peak at 1720 cm^{-1} corresponds to C=O stretching of ester, and the shoulder at 1700 cm^{-1} to C=O stretching of carboxylic group from maleic anhydride. The peak at 1460 cm^{-1} is due to $-\text{CH}_3$ bending and the broadening in the peak is due to *cis* C=C group. The peak due to $-\text{CH}_3$ bending exists at 1380 cm^{-1} , the peak at 1170 cm^{-1} corresponds to C–O–C stretching of ester, and the peak at 720 cm^{-1} is due to multiple CH_2 split from $(\text{CH}_2)_n$.

Both figures look similar, however, it can be noticed that in Fig. 3 the peaks at 3000 cm^{-1} has higher intensity and it is merged into the adjacent peak. This difference is due to the higher concentration of fatty acid residues with unsaturated bonds. The higher intensity of the peak below 1800 cm^{-1} shows the higher concentration of carboxylic groups from maleic anhydride. The higher intensity at 920 cm^{-1} is due to the higher dimer content because of the higher carboxylic acid groups.

Figs. 5 and 6 show the IR spectrum of the polyurethane produced by using MMG-I and MMG-II, respectively. The urethane bond was characterized by the presence of NH group at $3300\text{--}3500\text{ cm}^{-1}$. The peak at 2900 cm^{-1} is due to the CH stretching, and the peak at 1720 cm^{-1} corresponds to C=O stretching from ester groups. The other peaks are from the raw materials used. The absence of peaks in the range $2000\text{--}2300\text{ cm}^{-1}$ shows that all isocyanate groups were involved in the reaction, and that there are no significant isocyanate groups in the resin.

3.5. Color of the dry films

The varnish produced by using MMG-II, gave slightly yellow transparent films. On the other hand, the varnish produced from MMG-I gave brown and semitransparent films.

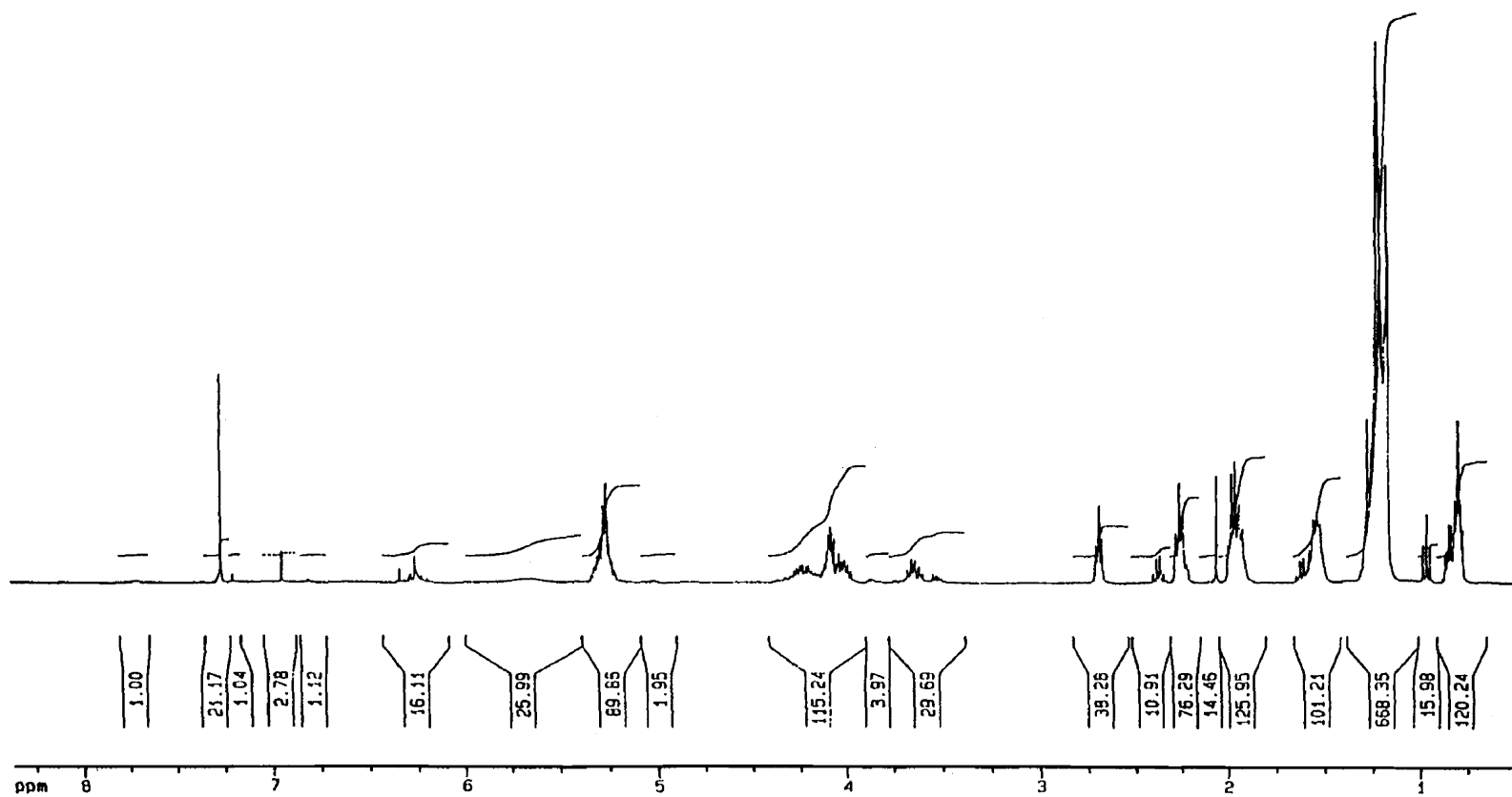


Fig. 1. NMR of monoglyceride and maleic anhydride mixture.

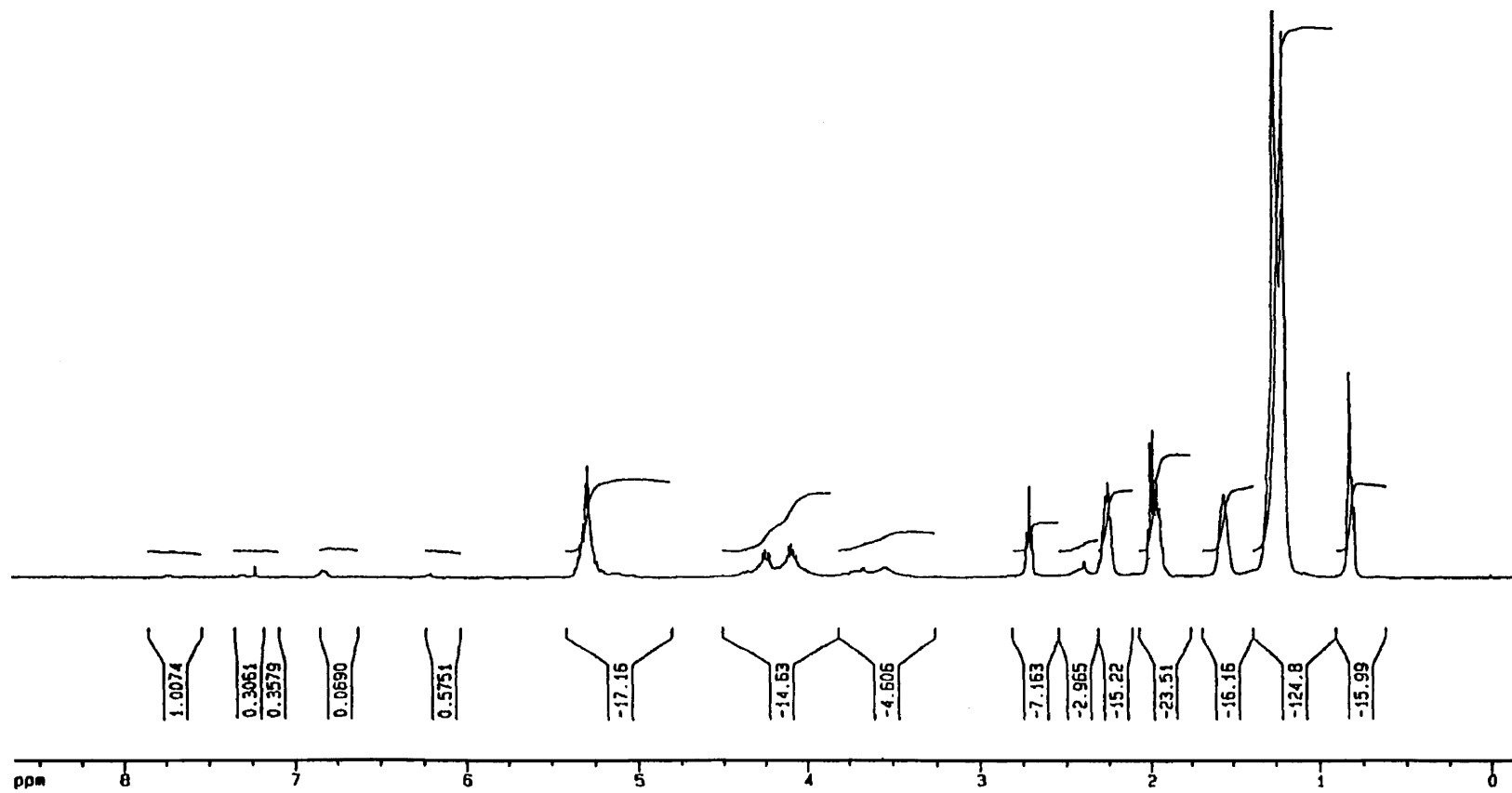


Fig. 2. NMR of MMG.

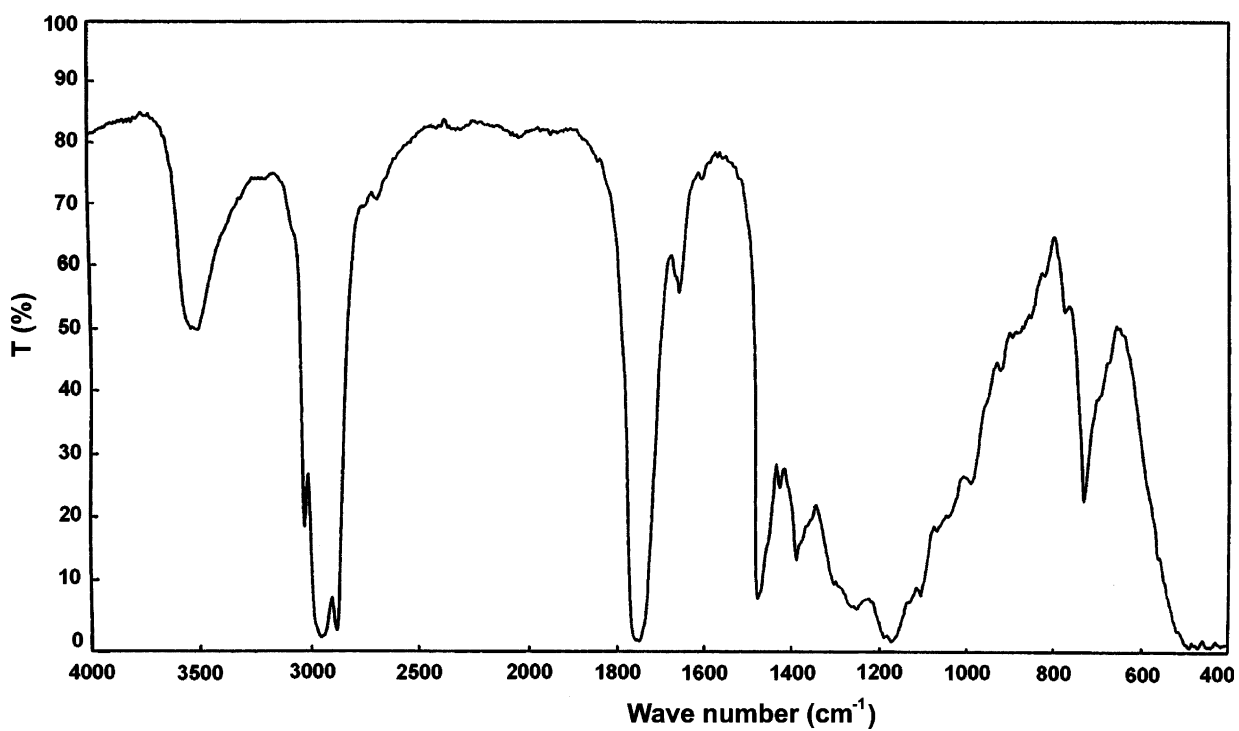


Fig. 3. IR of MMG produced by Method I.

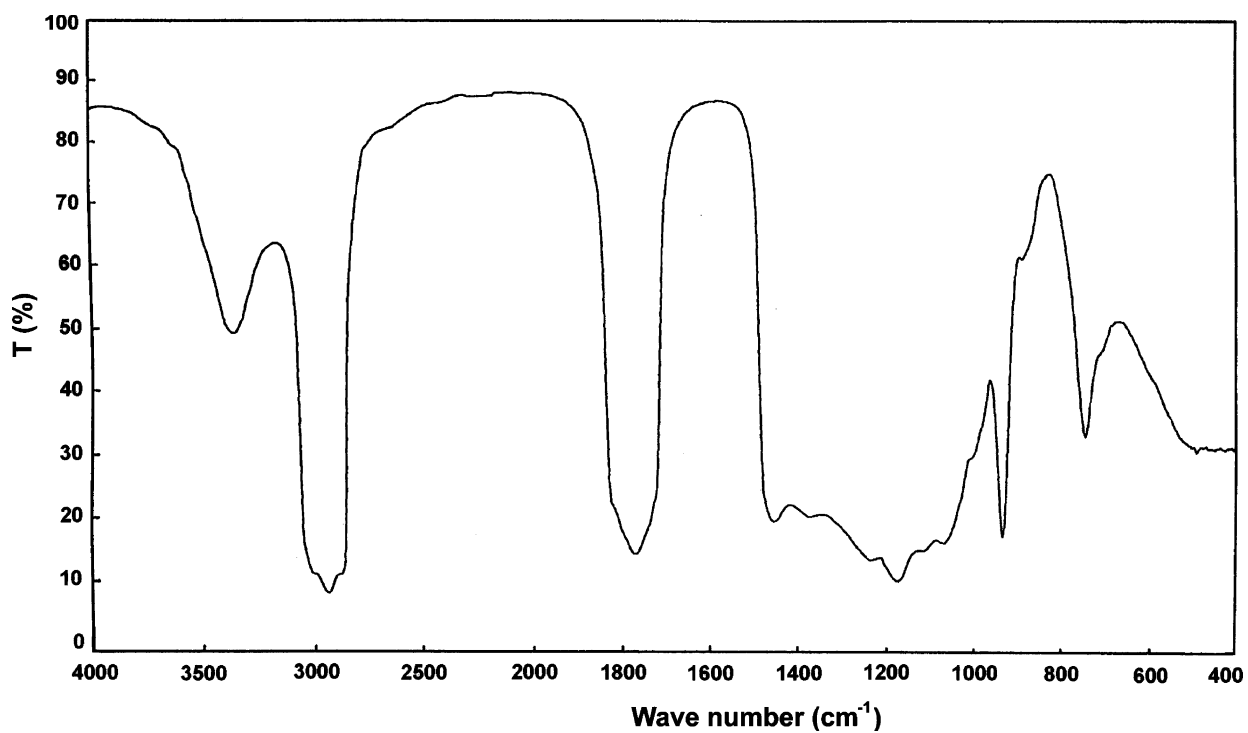


Fig. 4. IR of MMG produced by Method II.

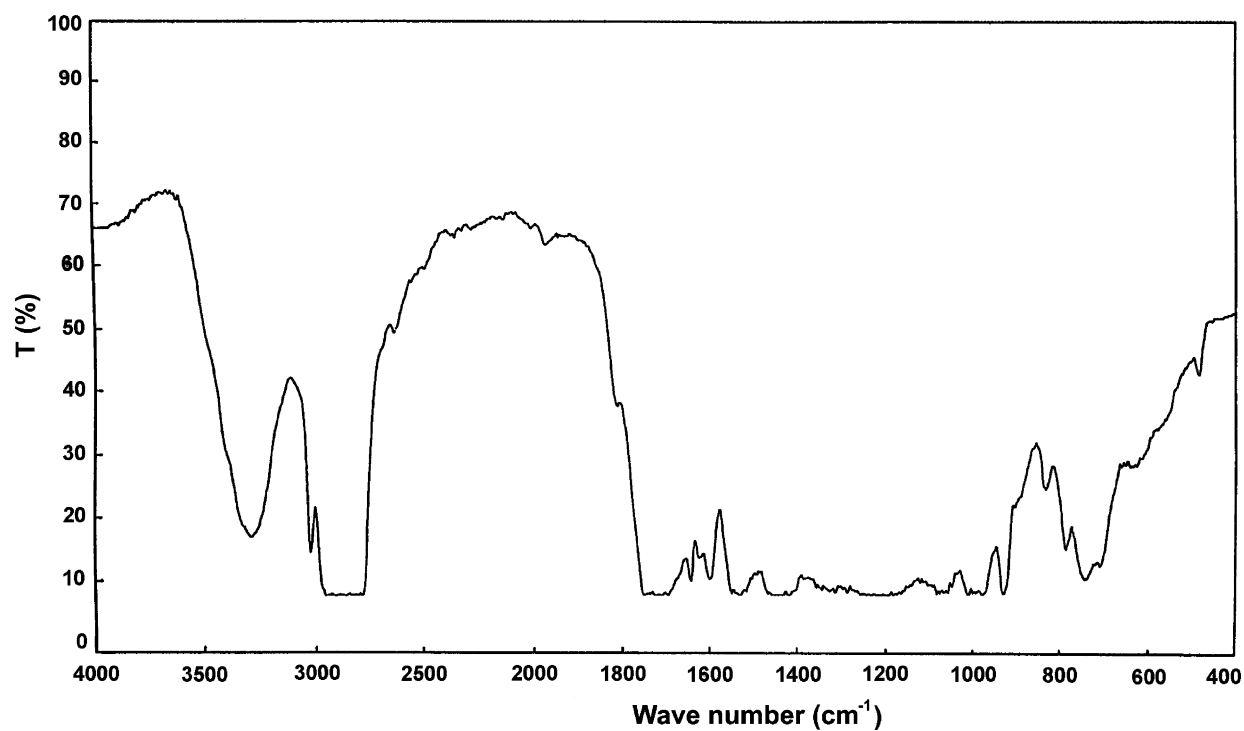


Fig. 5. IR spectrum of dry film of Sample A2.

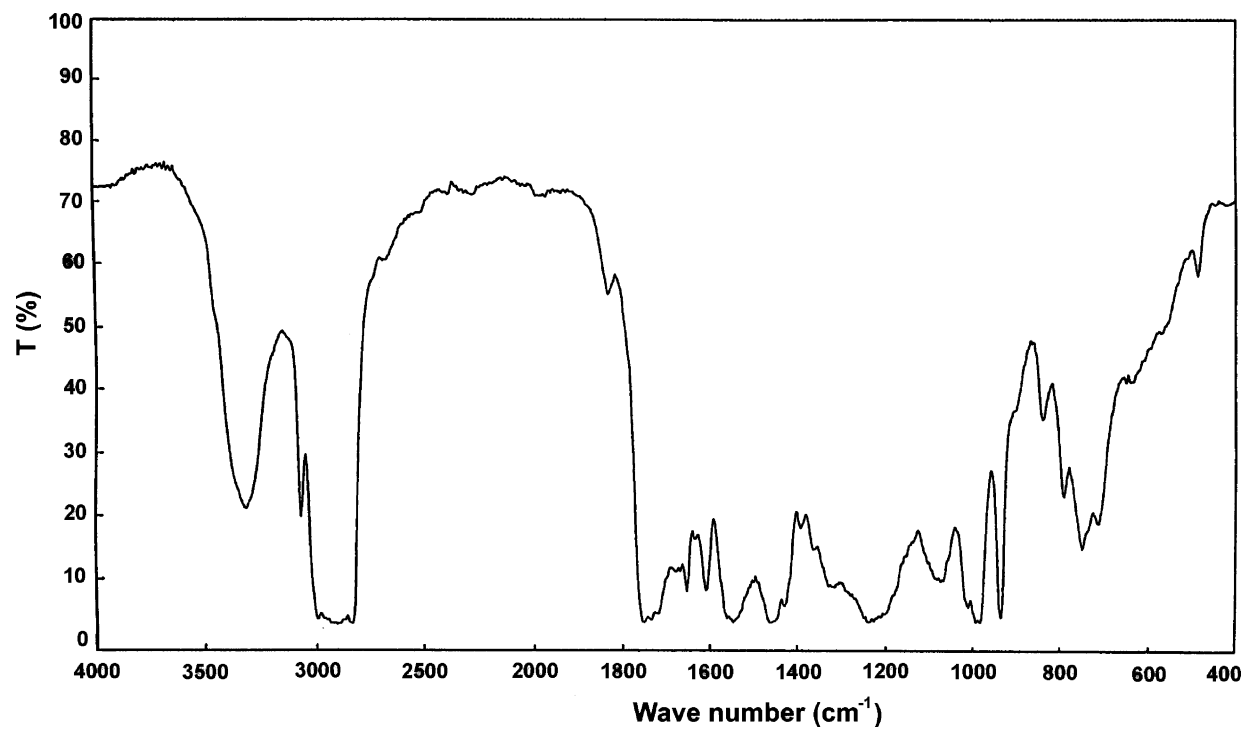


Fig. 6. IR spectrum of dry film of Sample B1.

Table 2
Gloss values for the samples

Method	Sample	Gloss value (%)		
		20°	60°	85°
I	A1	64.5	75.6	35.3
I	A2	21.0	53.2	48.0
I	A3	57.8	87.0	73.5
I	A4	25.5	55.0	49.2
II	B1	97.1	96.7	96.0
II	B2	86.8	90.3	95.0
II	B3	98.8	93.0	92.1
II	B4	78.3	89.0	87.3
II	B5	91.7	98.0	98.2

This difference is apparently due to higher ratio of fatty acid residues in the MMG produced by Method I.

3.6. Gloss test

A Rhopoint-Novoglass glossmeter was used to test the light reflection properties of the specimens. The gloss of dry films was measured at 20°, 60°, and 85°. The results were listed in Table 2. These results show that varnishes produced by using MMG-II had excellent gloss.

3.7. Hardness test

A Braive-Instrument Persoz Pendulum (No. 3034) was used. The principle of this test is based on the fact that the increase of hardness decreases the effect of friction, which increases the number of oscillations of the pendulum swinging on the test panel.

The dependence of hardness on the amount of MMG in the polymer can be seen in Figs. 7 and 8 for the varnishes produced by using MMG-I and MMG-II, respectively. In Fig. 7, the hardness decreases as the amount of MMG increases at all ratios used, while in Fig. 8 it first increases then decreases after 55% of MMG content. The decrease

of the amount of MMG results in a relative increase in the amount of HTPB. The double bond content of monoglyceride is about 1 per 9 carbon atoms and that of HTPB is about 1 per 4 carbon atoms. Therefore, HTPB gives denser cross-linking which results in higher hardness. It is also noticed that the varnish produced by using MMG-II has about twice higher hardness than that produced by using MMG-I. This is because MMG-I contains three fatty acid residues per molecule that makes the resin softer on drying whereas MMG-II contains only one fatty acid residue per molecule.

The decrease of hardness below 55% MMG in Fig. 8 can be due to the fact that hardness decreases with the increased branching. Branching in the polymer is due to the pendant fatty acid residues which come from MMG. The increase in the quantity of fatty acids increases side branches. There are two different cross-linkings which influence hardness: (i) the cross-linking due to double bonds of HTPB on the backbone and (ii) the cross-linking due to double bonds of fatty acid residues which are short branchings. As MMG decreases HTPB increases, so the double bonds on the backbone increase and the double bonds on the side branches decreases, or vice versa. The optimum ratio that balances both sources of hardness is 55% MMG in MMG-II containing varnish.

3.8. Mandrel bending test

A conical mandrel bending tester (Braive-Instruments No. 1510) was used. After coating the panels with the paint at a uniform thickness, they were fastened and bent over, and cracks were observed along the increasing radius of the conical mandrel. All samples passed bending test successfully without any cracks in the bent film. This is mainly due to the flexibility of the film which is a characteristic feature of polyurethanes.

3.9. Impact resistance test

A Gardner Impact tester (Model: 5510) was used for this test. A standard weight of (1+0.9 kg) was dropped on a film

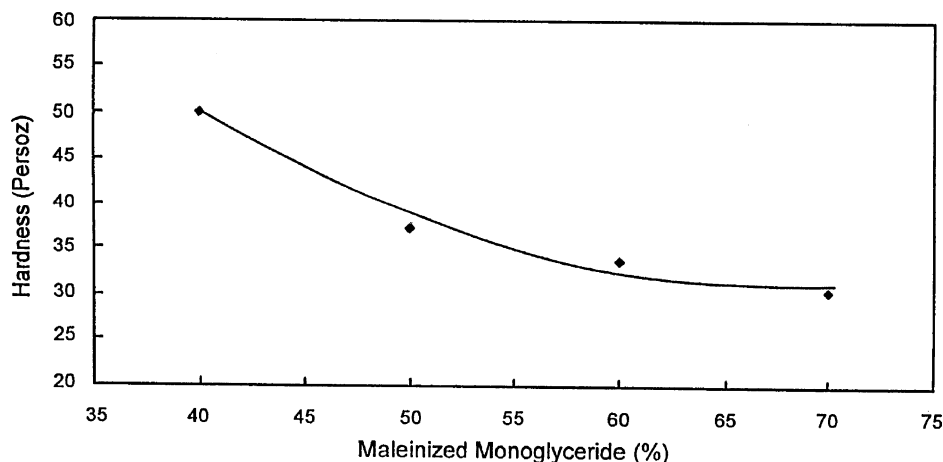


Fig. 7. Change of hardness with the percent of MMG-I in "MMG + HTPB".

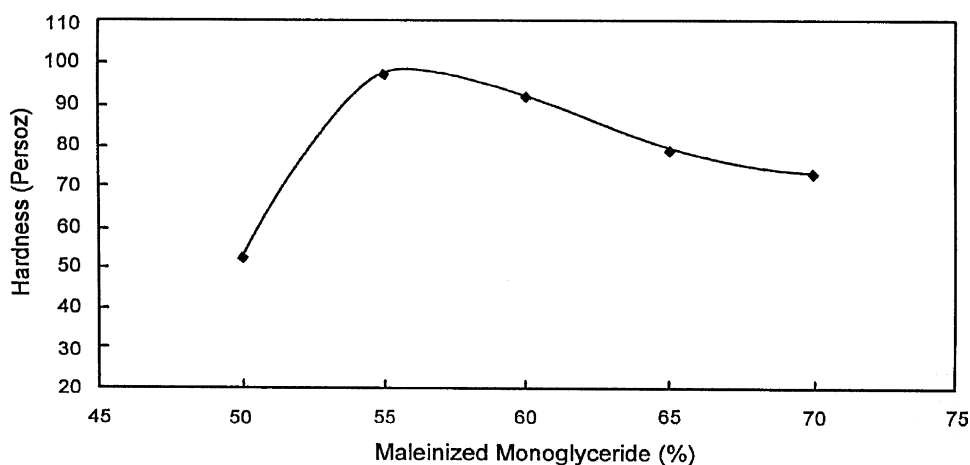


Fig. 8. Change of hardness with the percent of MMG-II in "MMG + HTPB".

coated on a metal plate from different heights. The impact value at which the film cracks is considered as the impact value for that sample. All tested samples showed resistance to impact up to 20 J which is the upper limit used without cracking.

3.10. Adhesion test

A crosshatch cutter was used to cut the film to produce a lattice pattern. After making a cross cut, the coating film was brushed with a soft tissue to remove any detached flakes of coating. Then, the pattern was checked according to ASTM D 3359 B. The maximum number of adhesion is "5" and the minimum is "0". Adhesion was tested on both a metal and a glass surface.

The adhesion test values for the samples are shown in Table 3. These results show that varnishes produced through Method I gives better adhesion than those produced through Method II. This is because MMG produced by Method I contains higher ratio of fatty acid residues, which improves adhesion. Also, it is obvious that Samples B1–B5 have better adhesion on metal plates than on glass plates.

Table 3
Adhesion test

Method	Sample	Adhesion number	
		Metal plate	Glass plate
I	A1	5 B	5 B
I	A2	5 B	5 B
I	A3	5 B	5 B
I	A4	5 B	5 B
II	B1	4 B	3 B
II	B2	5 B	0 B
II	B3	1 B	2 B
II	B4	1 B	1 B
II	B5	4 B	1 B

3.11. Abrasion resistance test

This test determines the resistance of coating film toward a falling abrasive. The abrasive is allowed to fall from a specified height through a guide tube onto a coated panel until the substrate becomes visible. The amount of abrasive per unit film thickness is reported as the abrasion resistance of the coating film. Silica sand was used as abrasive. All samples tested showed very good abrasion resistance and no significant loss in film thickness was observed.

4. Conclusions

1. The MMG-I containing varnish had darker color and lower gloss than the one that contains MMG-II.
2. In general, hardness showed a decreasing trend as the MMG ratio in the polyol increased.
3. The MMG-II-based varnish had higher hardness values than MMG-I-based varnish.
4. The optimum hardness in MMG-II-based varnish was achieved at 55% MMG ratio. This ratio may correspond to the optimum balance between the double bonds of HTPB and fatty acid residues.
5. The samples in which MMG-I was used showed much better adhesion compared to those in which MMG-II was used.
6. All samples tested for impact resistance showed resistance above 20 J.
7. All the tested samples passed conical mandrel bending test without any cracks.
8. No detectable loss in film thickness was observed after the abrasion resistance test.

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Processing and Properties of Palm Oil-Based Rigid Polyurethane Foam

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Abstract

Rigid polyurethane (PU) foam has been prepared from palm oil-derived polyol. The polyol was synthesized by transesterification reaction of palm oil and pentaerythritol using calcium oxide as a catalyst. The obtained palm oil-based polyol was reacted with commercial polymeric diphenylmethane diisocyanate in the presence of water (blowing agent), *N,N*-dimethylcyclohexylamine (catalyst) and polydimethylsiloxane (surfactant) to produce rigid PU foam. The effects of the amount of the catalyst and surfactant on foam properties (i.e. density, compressive strength and thermal behaviors) were studied. It was found that the density of the foams decreased whereas the compressive strength increased with the increasing amount of catalyst and that they were in the range of 38.7-59.0 kg/m³ and 193.6-268.4 kPa, respectively, while an increased amount of surfactant showed negligible effect on these two properties. Furthermore, TGA revealed that the degradation temperature of the prepared foams was about 377°C. Moreover, scanning electron micrographs showed that the cells of the obtained PU foams were closed cells. In addition, the foams were found to have higher number of cells as the concentration of catalyst increased, while the uniformity of cells increased with increasing amount of surfactant.

Keywords : palm oil, polyol, polyurethane foam

Introduction

Rigid polyurethane (PU) foam is an available material with the lowest thermal conductivity among foamed polymers used commercially.⁽⁴⁾ It has been widely utilized in the appliance and construction industry because of its excellent and unique combination of thermal insulation and mechanical properties. In addition, it is light in weight and versatile, and is employed increasingly in a variety of applications that include thermal and acoustic insulation, core materials for sandwich panels, fabrication of furniture, and flotation materials. PU foams perform well in most areas of low-temperature insulations. Products with density ranging from approximately 30 to 200 kg/m³ withstand temperatures down to -196°C.⁽²⁾ PU foam is usually synthesized by the reaction of diisocyanates with polyols. In general, blowing agent, catalyst and surfactant are also employed to regulate the properties and morphology of the cell structures. Most commercial diisocyanates and polyols are derived from petroleum which are

rapidly diminishing natural resources.⁽¹⁾ Between the two raw materials, to date only polyols can be synthesized from renewable resources such as oils, fats and starch. Several researchers have described the use of renewable raw materials for PU preparation. Some of them have investigated the possibilities of converting vegetable oils into polyols for producing PU foams. The Malaysian Palm Oil Board (MPOB) started producing polyol from epoxidized palm oil in the late 1980 s.^(5, 6) Chian, *et al.* (1998) used polyol derived from refined-bleached-deodorized (RBD) palm oil to produce rigid PU foam. The obtained PU foams provided a density of approximately 200 kg/m³ with compressive strength greater than 1 MPa. Salmiah, *et al.* (2001) indicated that palm oil-based polyols can be used for producing semi-rigid and rigid foams to be employed as insulators and wall- and ceiling-panels.

Each year, Thailand produces a large amount of palm oil not only for domestic consumption, but also for exportation. Due to the cheap and abundant supply of palm oil, the

potential use of polyol derived from palm oil as an alternative raw material for preparing rigid PU foam is possible. However, palm oil- which is a triacylglycerol produced by the palm trees- has no functional groups suitable to react with isocyanate to form urethane bonds.⁽¹⁾ In this work, treatment of palm oil with pentaerythritol produced a highly (OH) functionalized product. The chemical structure of the obtained polyol was characterized by FTIR technique. The rigid PU foam was prepared from the reaction of palm oil-based polyol and commercial polymeric diphenylmethane diisocyanate (PMDI) in the presence of water, N,N-dimethyl-cyclohexylamine (DMCHA) and polydimethylsiloxane (PDMS) as the blowing agent, catalyst and surfactant, respectively. In this study, the effects of catalyst content and surfactant concentration on the properties and morphology of the foams were investigated.

Experimental

Materials

Palm oil with acid value of 2, iodine value of 52 and specific gravity of 0.907 was obtained from Olene Co., Ltd. Pentaerythritol and PMDI (with isocyanate content of 31.4 wt%) were supplied by Siam Chemical Industry Co., Ltd. DMCHA was provided by South City Co., Ltd. and PDMS was donated by Thai Petrochemical Industry Co., Ltd. All materials were used as received without further purification. Preparation and characterization of palm oil-based polyol

Palm oil (200 g) in a 500 ml four-necked round-bottom flask, equipped with a stirrer, a thermometer, a condenser, a water separator, and N₂ gas inlet, was heated up to 150°C with stirring at the speed of 500 rpm under nitrogen atmosphere. Pentaerythritol (89 g) was added and the mixture was stirred and heated to 200°C followed by the addition of calcium oxide (0.15 g). The temperature was then raised to 245°C and the mixture was maintained at this temperature until a sample (1 part) was soluble in ethanol (3 parts). The obtained product was allowed to cool to room temperature under nitrogen atmosphere and its chemical structure was analyzed using an FTIR spectrophotometer (Perkin-Elmer FTIR System 200). The hydroxyl value was determined based on ASTM D 4274-94 Method C and the viscosity was determined using a Brookfield viscometer (Model RVT).

Preparation of Rigid PU Foam

The PU foams were prepared by adding PMDI to the polyol mixture, which consisted of a palm oil-based polyol, distilled water, DMCHA and PDMS with stirring at 1000 rpm using a high-speed mixer for 1 min. At the creamy stage (the mixture turning creamy), the mixture was poured into an open mold and allowed to rise freely. The cream time (the time from mixing to initiation of foaming) and rise time (the time from mixing to full expansion of foaming) were recorded. After that, the foam was removed from the mold and allowed to postcure for 2 days at room temperature before cutting into the test specimens.

Table 1 shows the chemical compositions of the PU foam samples. To investigate the effect of the catalyst and the surfactant contents on the properties of the PU foam, the amount of DMCHA and PDMS were varied from 0.25-1 php (parts per hundred polyol) and 2.5-10 php, respectively. The amount of polyol, PMDI, and distilled water were fixed at 100, 150, and 3 php, respectively.

Table 1. Chemical Compositions of Rigid Polyurethane Foam.

Sample	PMDI (g)	Polyol (g)	Distilled water ^a (g)	DMCH A ^b (g)	PDMS ^c (g)
1	60	40	1.2	0.1	1
2	60	40	1.2	0.2	1
3	60	40	1.2	0.3	1
4	60	40	1.2	0.4	1
5	60	40	1.2	0.1	2
6	60	40	1.2	0.2	2
7	60	40	1.2	0.3	2
8	60	40	1.2	0.4	2
9	60	40	1.2	0.1	3
10	60	40	1.2	0.2	3
11	60	40	1.2	0.3	3
12	60	40	1.2	0.4	3
13	60	40	1.2	0.1	4
14	60	40	1.2	0.2	4
15	60	40	1.2	0.3	4
16	60	40	1.2	0.4	4

^a 3 parts by weight based on 100 parts of the polyol.

^b 0.25-1 parts by weight based on 100 parts of the polyol.

^c 2.5-10 parts by weight based on 100 parts of the polyol.

Characterization and Property Measurements of PU Foam

The chemical structures of the obtained PU foams were characterized using an FTIR spectrophotometer (Perkin-Elmer FT-IR System 200). A scanning electron microscope (Jeol JSM-5900 LV) was used to examine the morphology of the foam. The accelerated voltage was 15 kV.

For density measurement, the PU foams were cut into specimens with dimensions of about $50 \times 50 \times 30$ mm (width $\times$ length $\times$ thickness). The exact dimensions were measured using a vernier caliper. The specimens were accurately weighed to determine their densities using the equation, density = mass/volume. The density for each foam was ascertained using the average value from six specimens.

The compressive strength of the foams was determined using an Instron Universal Testing Machine (LLOYD L500) with a load cell of 1.5 kN. The test was performed according to ASTM D 1621-00. The size of the specimen was $50 \times 50 \times 25$ mm (width $\times$ length $\times$ thickness), and the crosshead speed was 12.5 mm/min. The compressive stress at 10% deformation of its original thickness was calculated. The compressive strength for each foam was obtained using the average value from six specimens.

Thermogravimetric analysis (TGA) of the foams was performed using a thermogravimetric analyzer (Mettler Toledo TGA/SDTA 851e) at the temperature range from 35 to 800°C with the heating rate of 10°C/min under nitrogen atmosphere.

Results and Discussion

Characterization of Palm Oil-Based Polyol

The obtained palm oil-based polyol was a viscous yellowish liquid with viscosity of 355 poises which was much higher than that of the regular palm oil (60 poises). This high viscosity is due to hydrogen bonding associated with the hydroxyl groups. This polyol had a hydroxyl value of 385 mg KOH/g, which is suitable for rigid PU foam preparation.⁽⁷⁾

The FT-IR technique was employed to analyze the functional groups of palm oil-based polyol. Figure 1 shows the spectra of palm oil and palm oil-based polyol. The presence of hydroxyl group in the palm oil-based polyol is reflected by the transmittance peaks at wavenumbers of 3374 cm^{-1} , 1100 cm^{-1} (due to -OH in secondary alcohol) and 1050 cm^{-1} (due to -OH in primary alcohol). Furthermore, the obtained product was found to completely dissolve in ethanol. The results indicate that palm oil was converted into a highly (OH) functionalized product by transesterification reaction.

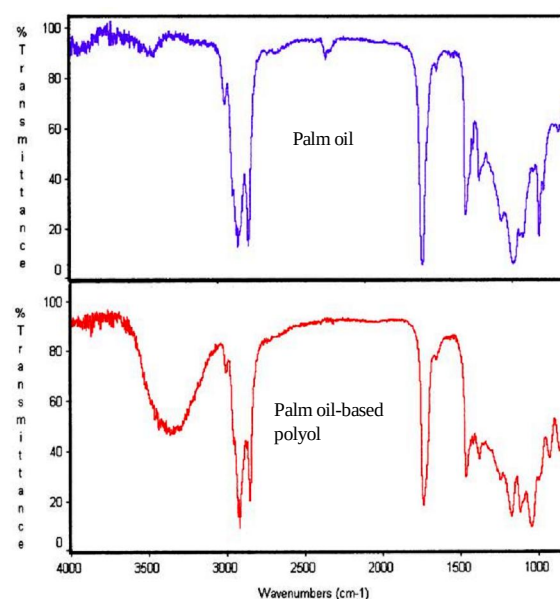


Figure 1. FTIR spectra of palm oil and palm oil-based polyol.

Preparation of Rigid PU Foam

When water is used as a blowing agent, a reaction occurs between the water and the isocyanate group to form an amine and carbon dioxide gas in the form of bubbles. After several seconds, the carbon dioxide produced in situ will diffuse into small air bubbles and enlarge them giving the mixture a creaming appearance. The time taken for the appearance to change, as measured from the initial mixing, is known as the cream time. As more carbon dioxide is generated, the bubbles expand and the foam begins to rise. While the bubbles are expanding, a polymerization reaction takes place in the liquid phase and the viscosity starts to increase. At full rise time, the reactions generating the gas stop. In this work, the

cream time and rise time varied in a range of 32–148 s and 179–529 s, respectively, as shown in Figures 2 and 3. Both the cream time and rise time of the prepared foams are longer than those of a typical rigid PU foam.⁽¹¹⁾ This phenomenon could be attributed to the secondary hydroxyl groups, which have lower reactivity existing in the palm oil-based polyol. It was previously found that an increase of the amount of catalysts in the foam formulation shortens the reaction time.⁽³⁾ This is in good agreement with our observation that the cream time and rise time of the prepared foams were reduced with increasing amount of DMCHA catalyst. On the other hand, as the amount of DMCHA remained constant, the increase in PDMS would slightly increase the cream time and rise time of the foams. This may be explained by the fact that increasing the surfactant level will effectively reduce functional group concentration. Consequently, the rate of foam rise and overall reaction rate are reduced.⁽⁸⁾ The results indicate that the catalyst plays an important role to control the foaming and curing rate of the rigid PU foam, whereas the surfactant seems to have only small effect on the foaming reaction.

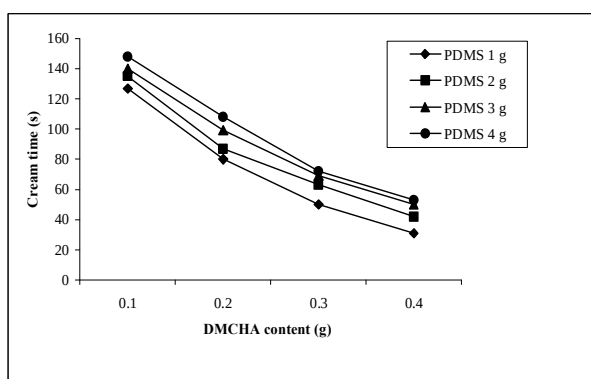


Figure 2. Cream time of rigid PU foams.

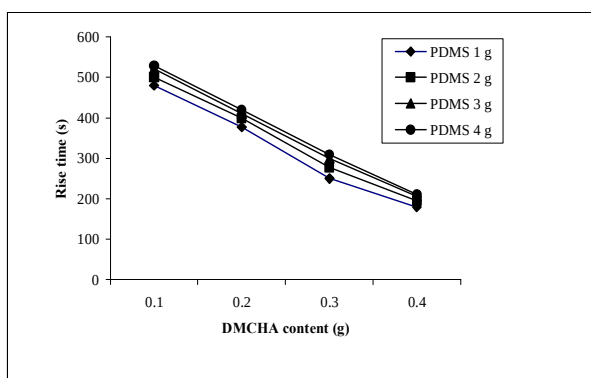


Figure 3. Rise time of rigid PU foams.

Characterization of PU Foam

The foams produced are very rigid and light weight. They are light yellow due to aromatic isocyanate content. However, we observed that the yellowness of the foams tends to be reduced with increasing amount of DMCHA.

The FTIR spectra of the PU foams prepared from palm oil-based polyol shown in Figure 4 and Figure 5 exhibit the characteristic peaks of urethane bonds at wavenumbers of 3385 cm^{-1} (-NH stretching), 1741 cm^{-1} (-CO stretching), 1514 cm^{-1} (-NH bending) and 1382 cm^{-1} (-OCONH asymmetric stretching). They also exhibit a characteristic peak of unreacted NCO groups at 2273 cm^{-1} . However, it can be seen (in Figure 4) that the intensity of these peaks decreases as the amount of DMCHA increases. This confirms the accelerated effect of the catalyst on the reaction of isocyanates with water and with polyols. On the other hand, Figure 5 shows that with various amount of PDMS, the intensity of the peaks corresponding to the NCO group is nearly the same. This suggests that the surfactant has no effect on the reaction rate.

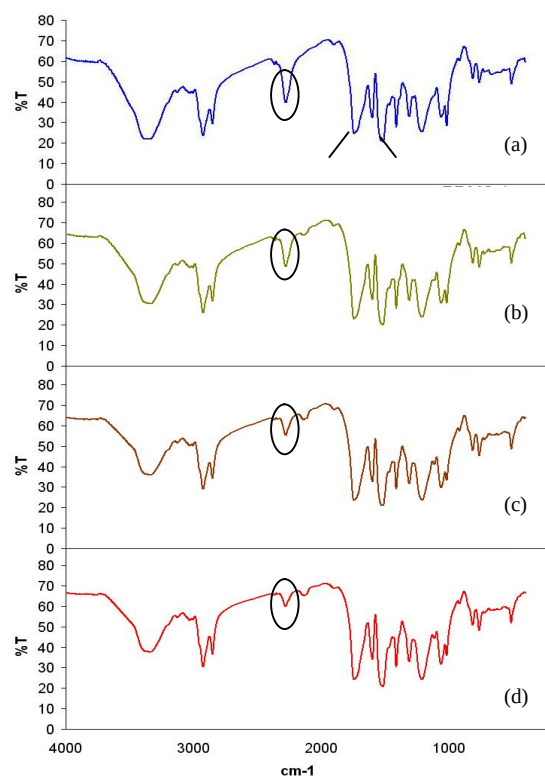


Figure 4. FTIR spectra of rigid PU foams prepared from 1 g PDMS and DMCHA (a) 0.1 g, (b) 0.2 g, (c) 0.3 g, and (d) 0.4 g.

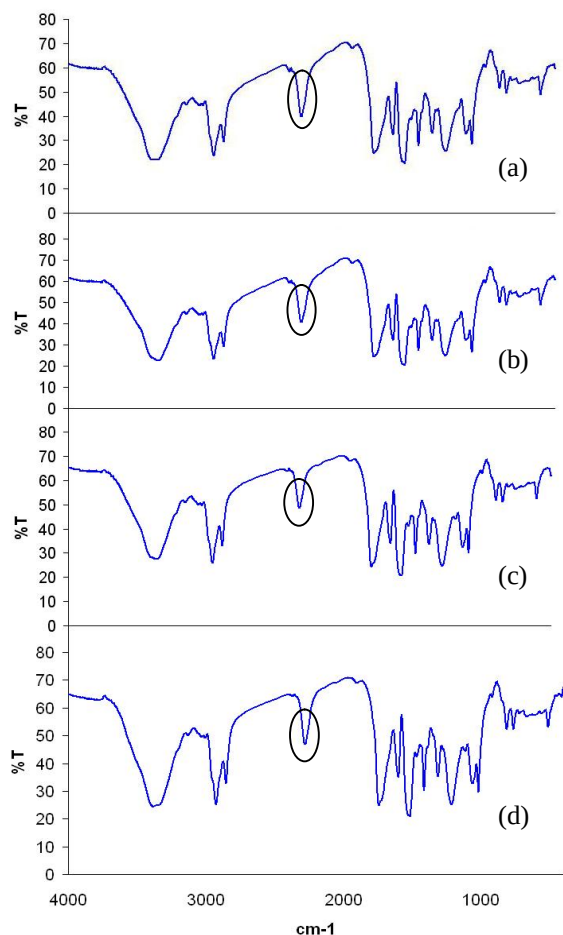


Figure 5. FTIR spectra of rigid PU foams prepared from DMCHA 0.1 g and PDMS (a) 0.1 g, (b) 2 g, (c) 3 g, and (d) 4 g.

Morphology of PU Foam

The cross-sectional surfaces of PU foam observed with scanning electron microscope (SEM) are shown in Figures 6 and 7. The shapes of the cells are spherical with many windows. The spherical shape cells are found to be closed cells. Figure 6 shows that the foams have a higher number of cells as the concentration of DMCHA increases. This indicates that more carbon dioxide gas has been generated at the higher level of catalyst and the number of closed cells will be increased. Figure 7 shows the micrographs of the PU foam samples with different PDMS contents. It is found that the cell size of PU foams decreases and the uniformity of the cells increases with increasing amount of surfactant. It is known that this silicone surfactant lowers the surface tension

between cells, and it stabilizes the cell walls (Seo, et al. 2002). The silicone surfactant prevents the coalescence of the cell, so it makes the cell size smaller.

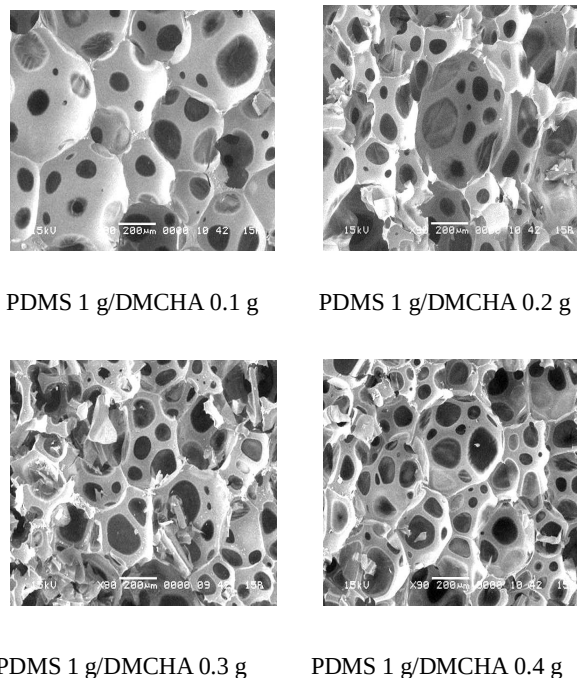


Figure 6. SEM micrographs of rigid PU foams with various amount of the catalyst.

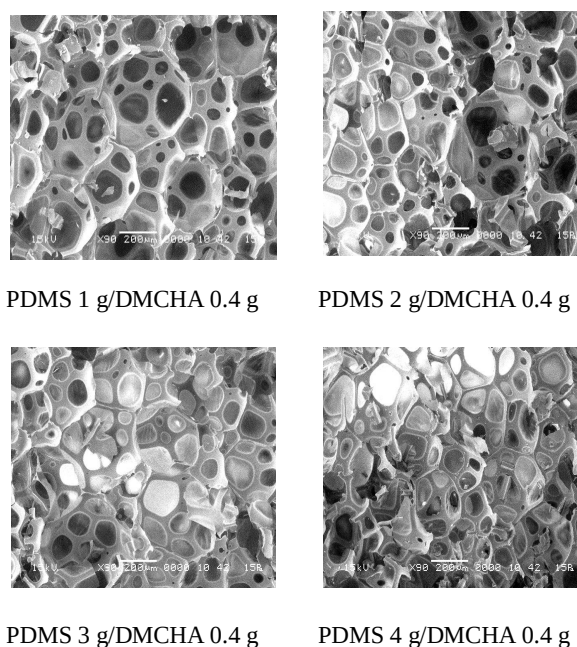


Figure 7. SEM micrographs of rigid PU foams with various amount of the surfactant.

Properties of PU Foam

The densities of the PU foams blown by distilled water are presented in Figure 8. It is found that when the DMCHA increases, the densities of the PU foams are decreased. This suggests that at a higher amount of catalyst, the foam rises more rapidly and causes a material of reduced density. On the other hand, the densities of the foams do not change significantly with the surfactant content.

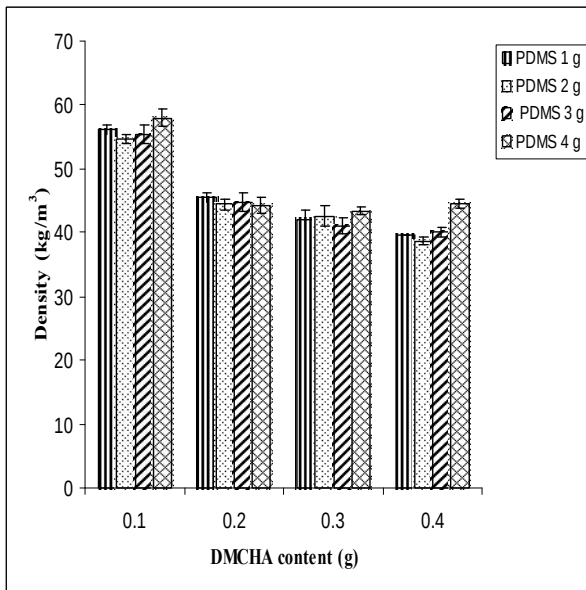


Figure 8. The effect of catalyst and surfactant on rigid PU foam density.

As shown in Figure 9, the compressive strength of the PU foams with various amount of DMCHA and PDMS is in the range of 194.6-268.4 kPa. It can be seen that the compressive strength decreases with an increase in DMCHA from 0.1 to 0.4 g at an equal content of PDMS. It is generally known that the mechanical properties of a cellular material mainly depend on its density. Therefore, when the amount of DMCHA is increased, the decrease of the compressive strength may be due to the decrease of foam density. On the other hand, if DMCHA is kept constant, the compressive strength of the PU foam is slightly different with various amount of PDMS. This indicates that the surfactant plays an insignificant role on the foam density as shown in Figure 8. Figure 10 shows the relationship between the compressive strength and the foam density. It can be clearly seen that density provides a significant effect on the compressive strength of the rigid PU foam.

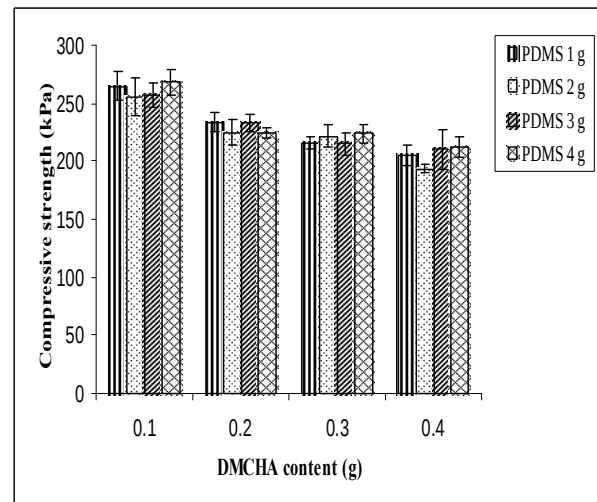


Figure 9. The compressive strength of rigid PU foams with various amount of the catalyst and surfactant.

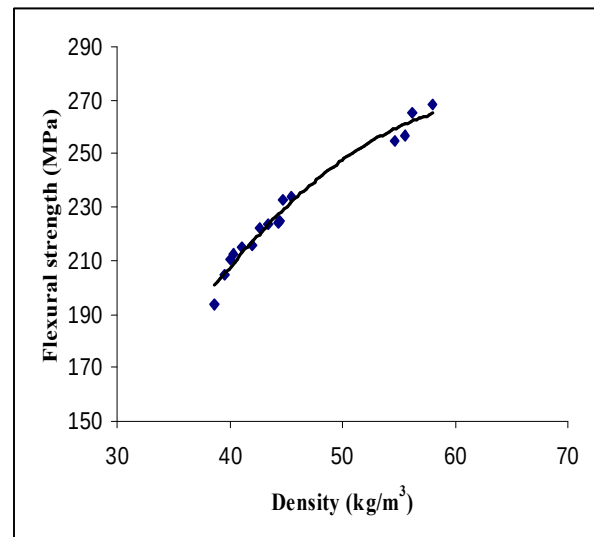


Figure 10. The compressive strength of rigid PU foams versus foam density.

It can be seen from the TGA thermogram as shown in Figure 11 that two stages of degradation occurred during heating. The first stage is at 285°C which may correspond to urethane bond break, while the second stage occurred at 377°C and may be due to polyol decomposition. All the rigid PU foams have approximately the same degradation temperature (Td).

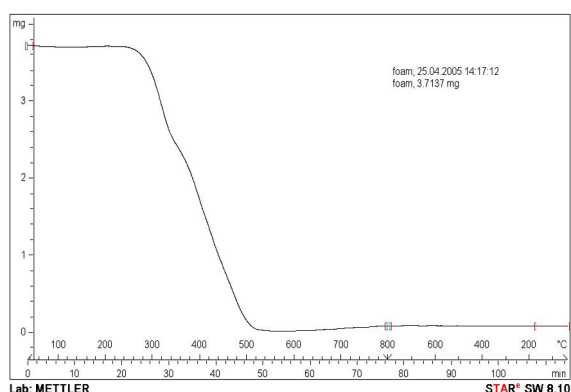


Figure 11. Example of TGA thermogram of rigid PU

Conclusion

The polyol based on palm oil could be used as one of the raw materials for preparing rigid polyurethane foams after transesterification of the palm oil with pentaerythritol. The prepared polyol was reacted with commercial PMDI in the presence of DMCHA catalyst and PDMS surfactant using distilled water as a blowing agent. The PU foams obtained exhibited densities and compressive strengths in the range of 38.7-58.0 kg/m³ and 194-268 kPa, respectively. The results of the morphology by SEM revealed that the cells of these foams were closed cells. Increasing catalyst content in the foam formation shortens the reaction time and increases the number of cells and compressive strength. Meanwhile, the surfactant seems to have only small effect on the foaming reaction and properties of the foam. From TGA results, all the rigid PU foams have approximately the same degradation temperature of about 377°C.

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

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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).

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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 1 Mono-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.

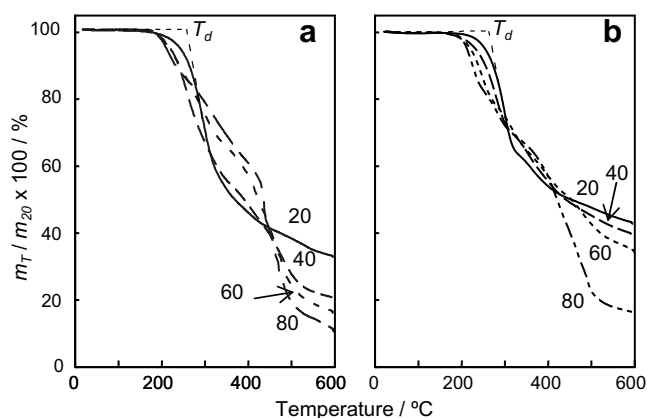


Fig. 1. TG curves of the PEG- or DEG-contained foams having various PO-p contents as indicated on each curve (%): (a) PEG; (b) DEG.

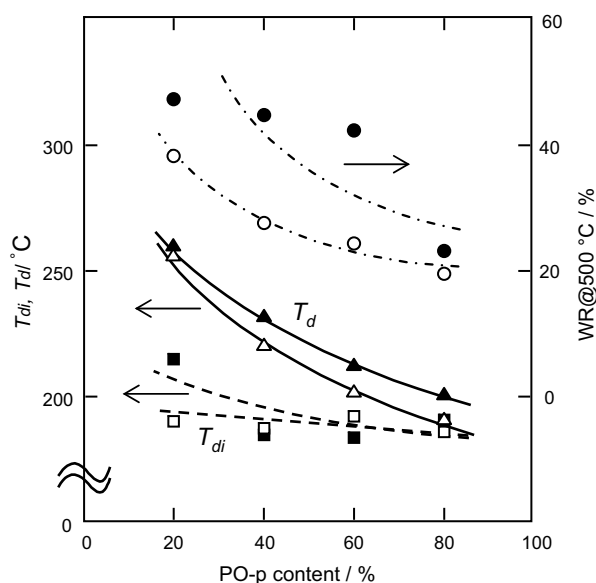


Fig. 2. Starting (T_{di}) and thermal decomposition (T_d) temperatures and weight residues (WR@500 °C) of PU foams having various PO-p content; PEG series: open symbols; DEG series: closed symbols.

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

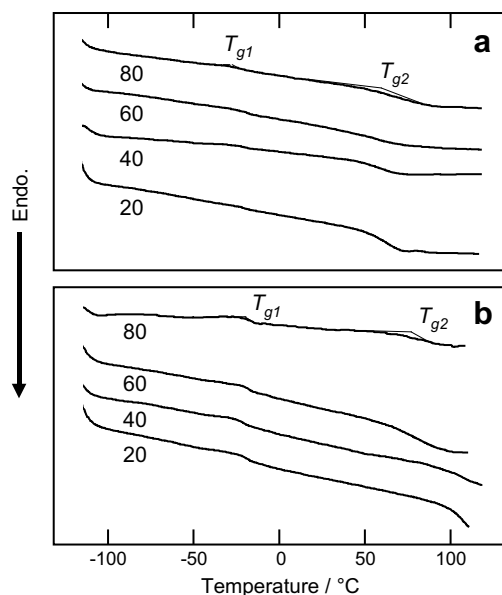


Fig. 3. DSC curves of the PEG- or DEG-containing foams having various PO-p contents as indicated on each curve (%): (a) PEG; (b) DEG.

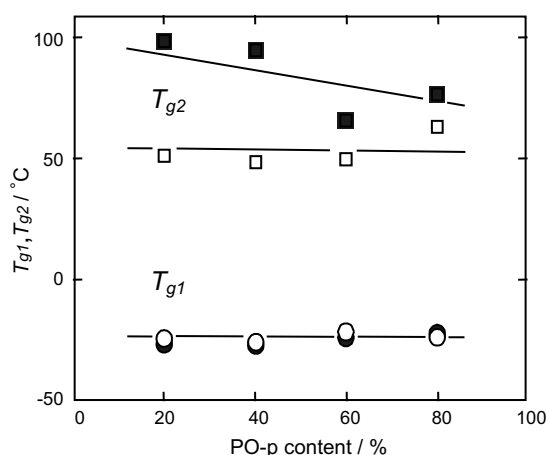


Fig. 4. Relationship between glass transition temperatures (T_{g1} and T_{g2}) and PO-p content; PEG series: open symbols; DEG series: closed symbols.

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

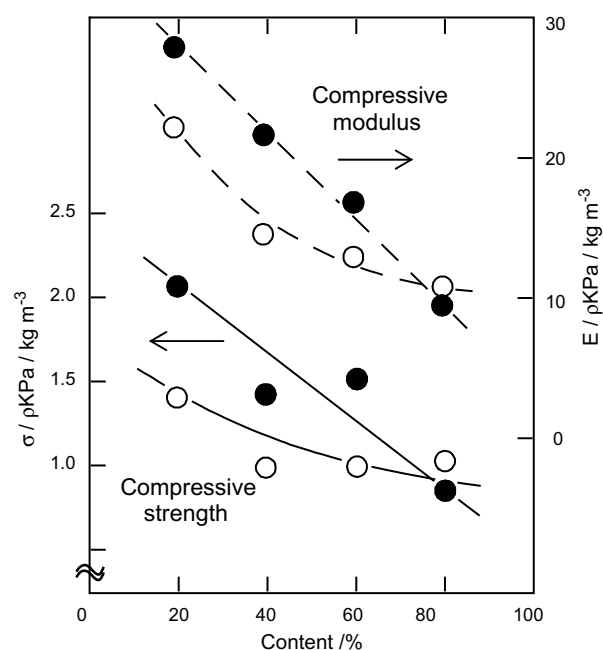


Fig. 5. Changes of compressive strength (σ/ρ) and compressive modulus (E/ρ) along PO-p content; PEG series: open symbols; DEG series: closed symbols.

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.

Acknowledgements

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THERMAL ANALYSIS OF SOYBEAN OIL BASED POLYOLS

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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

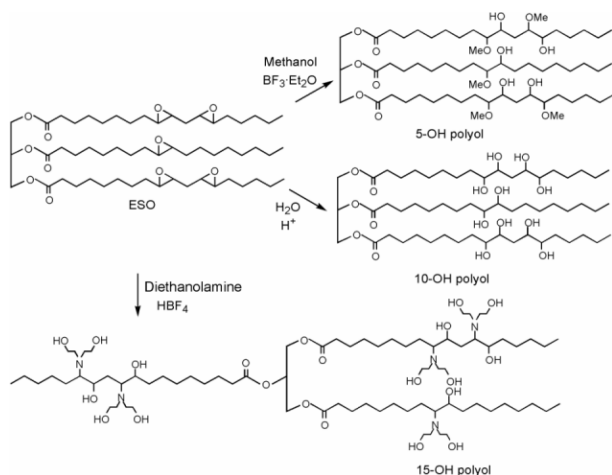
The epoxidized soybean oil (ESO) used in this research was kindly supplied by Nanhai Oil Co. Ltd. with a molecular mass of 985 (ESI-MS) and with a 4.375 mol kg⁻¹ epoxy oxygen content. Deuterated acetone (D, 99.9%) was supplied by Cambridge Isotope Laboratories, Inc., Andover, MA, USA. Diethanolamine [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-

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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 N₂ 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°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 CH₃OH, H₂O and NH(CH₂CH₂OH)₂ caused a shift and deformation of the melting peak. Hydroxyl groups were introduced in this chemosynthesis reac-

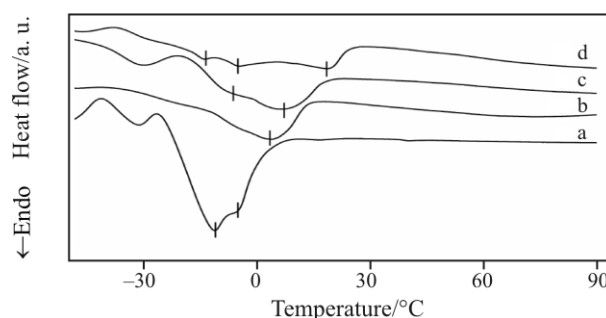


Fig. 1 DSC curves of soy based polyols; a – ESO; b – 5-OH polyol; c – 10-OH polyol; d – 15-OH polyol

Table 1 Melting point of ESO and polyols

Peak	T/°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

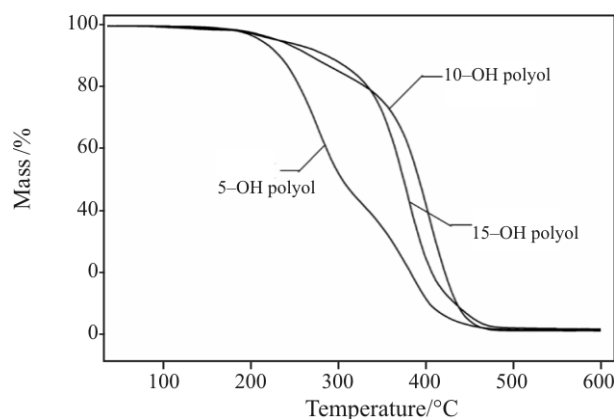


Fig. 2 TG profiles of polyols at 10°C min⁻¹ under nitrogen atmosphere

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.

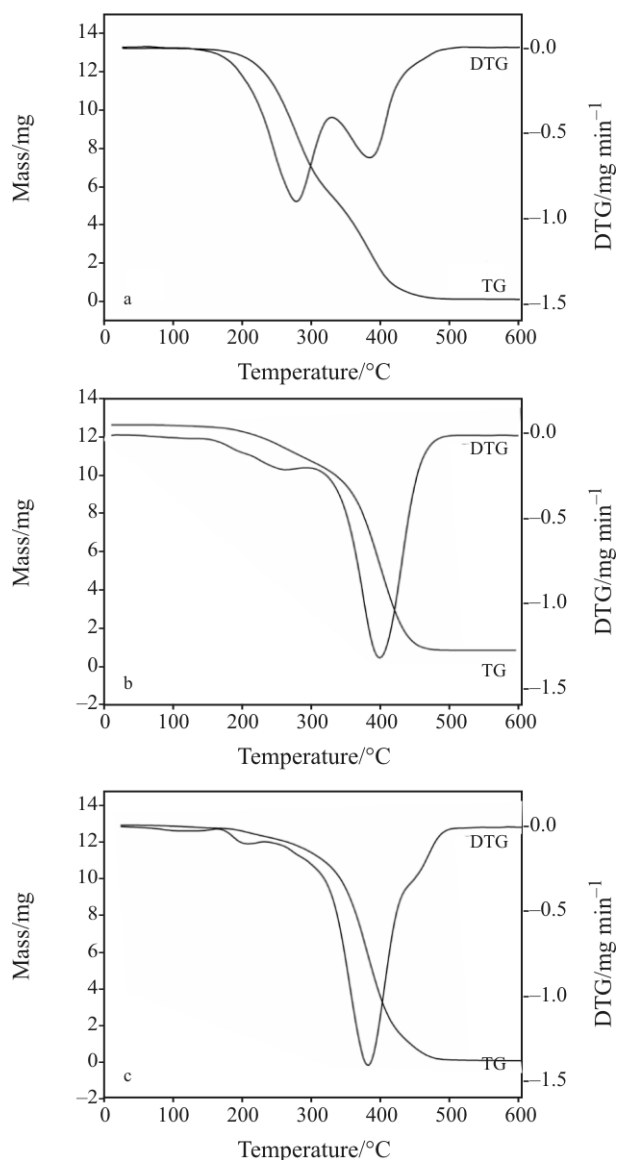


Fig. 3 TG and DTG curves obtained using a heating rate of $10^{\circ}\text{C min}^{-1}$ under dynamic nitrogen atmosphere with a flow rate of 30 mL min^{-1} ; a – 5-OH polyol, b – 10-OH polyol, c – 15-OH polyol

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 $\beta=10^{\circ}\text{C min}^{-1}$

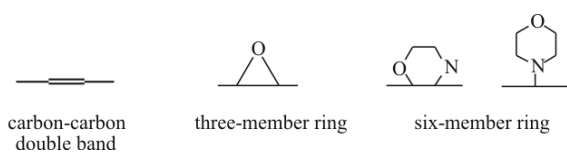
Project	5-OH polyol	10-OH polyol	15-OH polyol
Onset $T/^{\circ}\text{C}$	233.4	218.4	186.8
Primary region $T/^{\circ}\text{C}$	160–324	150–316	163–233
Primary mass loss/%	45.45	16.72	3.56
Secondary region $T/^{\circ}\text{C}$	324–512	316–509	233–425
Secondary mass loss/%	41.83	82.24	83.59
Tertiary region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

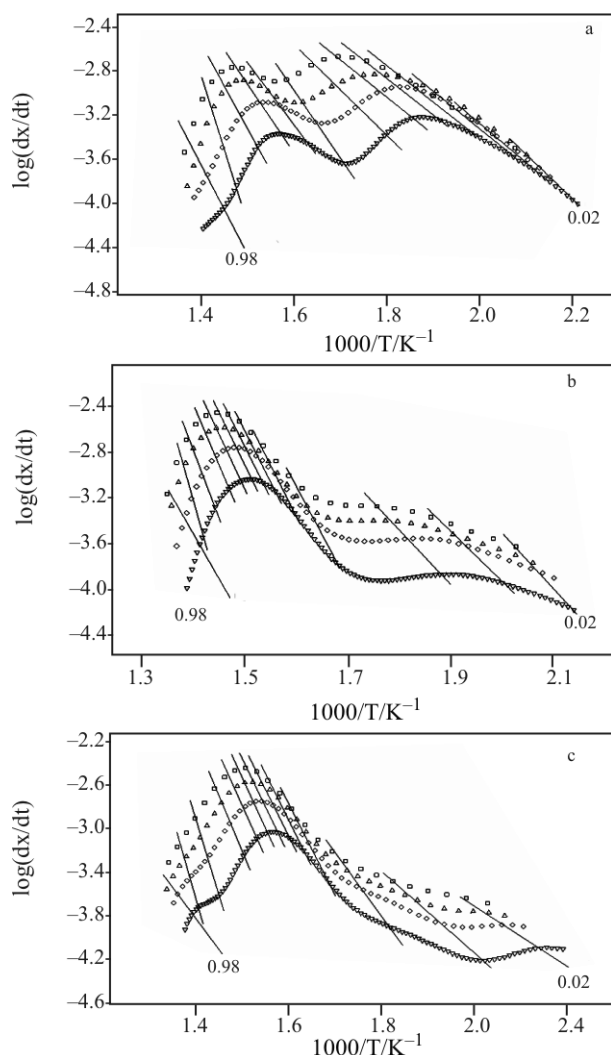


Fig. 4 Friedman's analyses of: a – 5-OH polyol; b – 10-OH polyol; c – 15-OH polyol

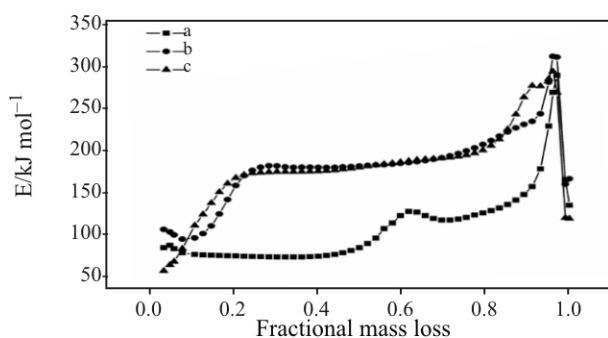


Fig. 5 Activation energy plotted from Friedman's analyses: a – 5-OH polyol; b – 10-OH polyol; c – 15-OH polyol

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.

Acknowledgements

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A THERMOANALYTIC AND KINETIC STUDY OF SUNFLOWER OIL

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Abstract - Recently, thermoanalytic methods have frequently been used in the characterization of oils and fats. In this work, thermoanalytic and kinetic parameters of sunflower oils, with and without antioxidants, were evaluated using thermogravimetry / derivative thermogravimetry and differential scanning calorimetry. The thermogravimetric profiles for the sunflower oils had similar characteristics, showing a level stretch indicative of stability up to about 200°C. Thermal decomposition of these oils occurred in three stages, related to the decomposition of polyunsaturated, monounsaturated and saturated fatty acids, respectively. DSC curves show two events that characterize the polymerization and decomposition of triglycerides. The heat capacities of the sunflower oils, obtained by DSC, showed a good correlation and were dependent on the composition of fatty acids. The kinetic parameters, obtained by non isothermal thermogravimetry by the Coats and Redfern, Madhusudanan, Horowitz and Metzger and Van Krevelen methods, were dependent on the antioxidant used. Increasing the frying time produced a decrease in the onset of thermal decomposition temperature in the sunflower oils analyzed.

Keywords: sunflower oil, thermogravimetry, kinetics.

INTRODUCTION

Edible vegetable oils are highly appreciated for culinary uses because of the properties they impart on food, and technicians and experts have been called on to develop new analytical methods capable of evaluating processing and storage conditions (Felsner and Matos, 1998). These products deteriorate when processed inadequately, with the principal decomposition reaction being oxidation. Oxidation of the oils occurs through a free radical mechanism, initially characterized by the emergence of a sweetish and unpleasant odor, which becomes progressive worse until attaining the characteristic

smell of rancid fat, i.e., the decomposition of hydroxides and peroxides in low molecular weight acids and aldehydes occurs (Gennaro et al., 1998).

Frying is one of the most commonly used methods of food preparation in the home and in industry, and the prolonged use of oil for this purpose causes changes in its physical and/or chemical properties (Moretto and Fett, 1998).

Several methods have been proposed to evaluate the quality of edible oils (Felsner and Matos, 1998). Most of these methods submit a sample to conditions that accelerate the normal oxidation process. The older methods used to estimate the quality of vegetable oils cause deterioration by maintaining the

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sample at elevated temperatures in contact with air and then periodically weighing to verify the gain in mass or examining organoleptically for rancidity. The peroxides or other oxidation products formed can be determined by spectral or chemical analysis (Kowalski, 1989). Some of the frequently used tests employed to predict the quality of vegetable oils are the periodic determination of peroxide index, the active oxygen method (AOM), the automated AOM method and the oxygen pump method (Lee and Min, 1990). Currently, thermoanalytic methods such as differential scanning calorimetry (DSC) and thermogravimetry / derivative thermogravimetry (TG/DTG) are receiving considerable attention. TG/DTG curves can be used to estimate the quality of edible oil by determining the kinetic parameters (Santos et al., 2001; Santos et al., 2002) and the oxidative induction period. On the other hand, as the oxidative thermal decomposition involves exothermic and endothermic reactions, it is possible to estimate the energy involved in the determination process by thermal techniques such as DTA and DSC. Therefore, these methods are more advantageous than the conventional methods, because they are more precise and sensitive and require a smaller sample mass and results are obtained more rapidly (Souza et al., 1998).

In view of these advantages, it becomes indispensable to analyze the stability of these oils during thermal treatment (frying) and storage. The thermoanalytic (specific heat, stability, decomposition enthalpy) and the kinetic (activation energy, frequency factor, order of reaction) parameters were determined in this study; deterioration of sunflower oil under frying conditions was also studied with the use of differential scanning calorimetry and non isothermal thermogravimetry, in an atmosphere of nitrogen and air, respectively.

EXPERIMENTAL

Materials

Samples of edible sunflower oils with and

without artificial antioxidants, acquired at a local market and produced by Brazilian industry, and having the composition listed in Table 1, were used in the study.

Thermal Analysis

The non isothermal TG/DTG curves were obtained in a Shimadzu TGA-50 thermobalance in air (20 mLmin⁻¹), using an alumina crucible with heating rates of 2, 5, 10 and 20°Cmin⁻¹ and a sample mass of 8.0±0.5mg in a temperature range of 25 to 800°C.

The DSC curves were obtained in a Shimadzu DSC-50 differential scanning calorimeter, in nitrogen (50 mLmin⁻¹) using an alumina crucible with heating rates of 5, 10 and 20°Cmin⁻¹ and a sample mass of 8.0±0.5mg in a temperature range of 25 to 500°C.

Specific Heat Measurement

The heat capacities of the sunflower oils were determined from the data obtained by DSC. The calculations were based on implementation of the temperature program. The oil samples were heated at a rate of 5°Cmin⁻¹ up to 30°C during five minutes. Then, they were heated at a rate of 10°Cmin⁻¹ up to 200°C during five minutes.

The following ratio was used to calculate the heat capacities:

$$c = \frac{m_0 c_0}{m} \cdot \frac{S_3 - S_1}{S_2 - S_1} \quad (1)$$

where c_0 and c are the specific heat of the reference material and of the sunflower oil, respectively; m_0 and m refer to the mass of samples and of the reference material, respectively, and S_1 , S_2 and S_3 are the thermal displacements of the DSC in relation to the blank, reference and sample, respectively (Kasprzycka-Guttman et al., 1995).

Table 1: Compositions of the sunflower oils analyzed.

Composition	Sunflower Oil A	Sunflower Oil B
Monounsaturated (%)	22.8	23.0
Polyunsaturated (%)	65.2	65.0
Saturated (%)	12.0	12.0
Artificial antioxidant	Citric acid	—

Kinetic Study

The theoretical basis for the kinetic calculations by non isothermal thermogravimetry is expressed in the following equation:

$$g(\alpha) = \frac{A}{\phi} \int_0^T \exp\left(-\frac{E_a}{RT}\right) dT \quad (2)$$

where A is the frequency factor, T is the temperature, R is the universal gas constant, ϕ is the heating rate and E_a is the activation energy. This mathematical equation describes the thermogravimetric curve, where $g(\alpha)$ represents the reaction mechanism and the second term in the equation can not be solved analytically; it can only be solved by approximation numerical methods. Various approximations for calculation of this integral have been proposed, giving rise to the different methods for determining kinetic parameters from thermogravimetric curves (Guo and Lua, 2000).

The integral methods proposed by Coats and Redfern and Madhusudanan and the approximation methods proposed by Horowitz and Meltzger and Van Krevelen were used in this study (Coats and Redfern, 1964; Horowitz and Meltzger, 1963; Madhusudanan et al., 1993; Van Krevelen et al., 1951).

Thermal Degradation

The study of thermal degradation of sunflower oils was carried out by thermogravimetric measurement. For this purpose the oils were heated

to 190°C for periods of 0.5, 4.0 and 8.0 h. The sunflower oils were heated in a 500 mL flask with a surface diameter of about 4 cm that was exposed to air. Afterwards, TG/DTG curves were obtained in a Shimadzu TGA-50 thermobalance in air (20 mLmin⁻¹) at a heating rate of 5°Cmin⁻¹ with the objective of verifying of influence the frying time and temperature on the thermal stability of sunflower oils.

RESULTS AND DISCUSSION

Thermal Behavior

The thermal decomposition profiles for the sunflower oils have similar characteristics, as can be observed in Figs. 1 and 2, where all the non isothermal TG/DTG curves have three thermal decomposition steps in the range of 230 to 550°C, with no residue remaining at 800°C. Thermal decomposition of these oils occurred in three stages, related to the decomposition of polyunsaturated, monounsaturated and saturated fatty acids, respectively.

In relation to the thermal decomposition steps, it was observed that the first step (230 to 380°C) corresponds to the decomposition of the polyunsaturated fatty acids. During heating, the triglycerides, which form 96 to 98% of the edible oils, produce volatile compounds, which are constantly removed by vapor generated during heating. These products (dimers, trimers, polymers) are formed principally by thermal reactions of unsaturated fatty acids, such as linoleic acid.

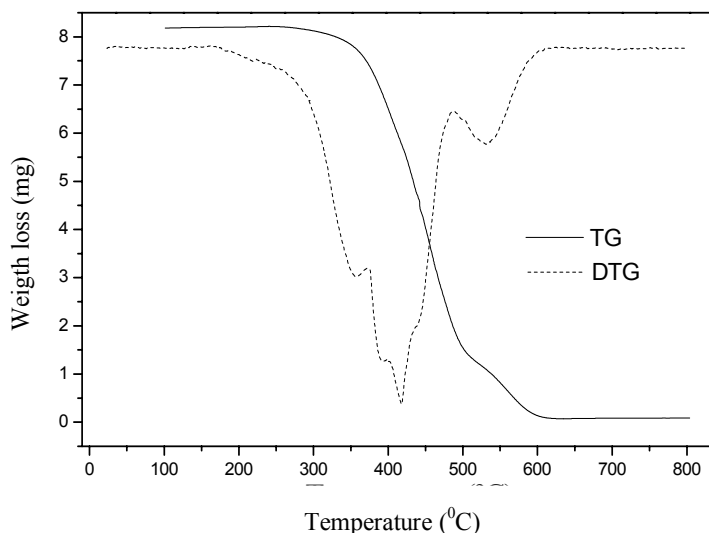


Figure 1: TG/DTG curves for sunflower oil with artificial antioxidants.

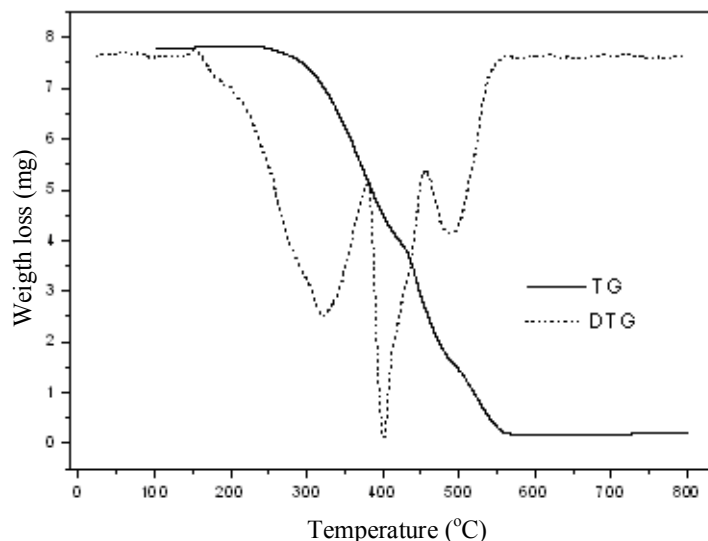


Figure 2: TG/DTG curves for sunflower oil without artificial antioxidants

The first step is the most important for the thermal stability of edible oils, because this is the step where decomposition of the unsaturated fatty acids begins. On the basis of the temperature at the beginning of thermal decomposition, it can be established that sunflower oil A, containing the antioxidants citric acid and vitamin E, had a higher thermal stability than that observed for sunflower oil B. Thus, it can be verified that the thermal stability of sunflower oils is dependent on the composition of the fatty acids, as it is influenced by artificial antioxidants.

The beginning of oxidation in edible vegetable oils is characterized by absorption of oxygen through the fatty acid chain, subsequently forming the oxidation product as peroxides. This behavior is generally identified by an increase in the initial mass of the sample. For the sunflower oil samples analyzed in air, a small gain in mass in the DTG curve for oil B was observed (Fig. 2), indicating that the process of thermal decomposition involved the absorption of oxygen as well as the liberation of volatiles. This was not observed for sunflower oil A (Fig. 2), where the reaction resulted only the liberation of volatiles.

The second step in the thermal decomposition of sunflower oils (380 to 480°C) corresponds to the decomposition of monounsaturated fatty acids, such as oleic acid. During this reaction, the double bonds are broken, causing the triglyceride molecules in the edible vegetable oils to become saturated. The third step in the thermal decomposition, which occurs in a temperature range of around 480 to 550°C, corresponds to the thermal decomposition of saturated fatty acids, such as palmitic acid.

To verify the dependence of the thermogravimetric profile for sunflower oils on experimental factors, the heating rate was varied from 2 to 5, 10 and 20°Cmin⁻¹, as shown in Fig. 3. It can be observed (Fig. 3) that there is a displacement in the initial decomposition temperature with the increase in heating rate. The thermal decomposition occurred in three steps at the heating rates 2, 5 and 10°Cmin⁻¹, whereas at 20°Cmin⁻¹ only two events corresponding to thermal decomposition were observed. This was probably due to the superposition of the steps.

DSC curves (see Fig. 4) for sunflower oils have similar profiles, verifying the endothermic and exothermic transitions. The exothermic transitions probably correspond to polymerization of a fatty acids component of the sunflower oils, occurring at around 340°C, whereas the endothermic transitions refer to thermal decomposition of saturated and unsaturated fatty acids, component of the vegetable oils, in agreement with the thermogravimetric results. The increase in heating rate produces a broadening and, consequently, an increase in the area of the peaks corresponding to the thermal decomposition of these oils. As the events observed refer to chemical processes, the increase in heating rate results in the decomposition of a larger quantity of fatty acids.

The enthalpies involved in the thermal decomposition process, observed in the DSC curves correspond to the molar enthalpies of polymerization and decomposition and have differentiated values, as shown in Table 2. These results indicate that the polymerization and decomposition enthalpies are directly related to the fatty acids composition of sunflower oils.

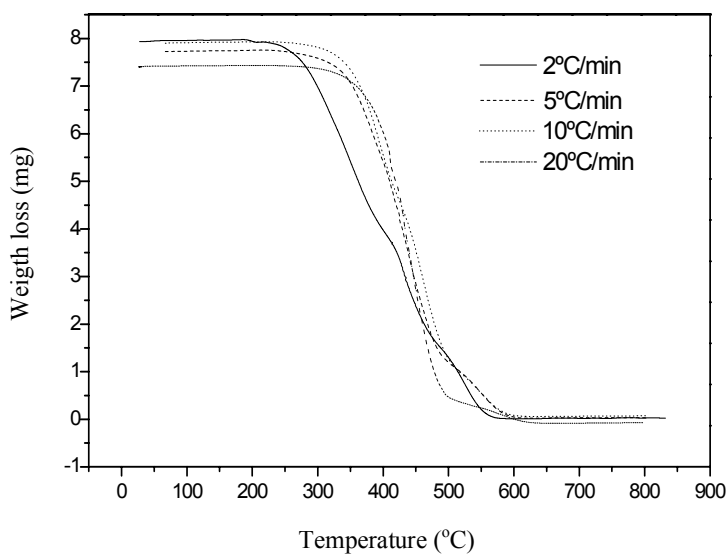


Figure 3: TG curves for sunflower oils at different heating rates.

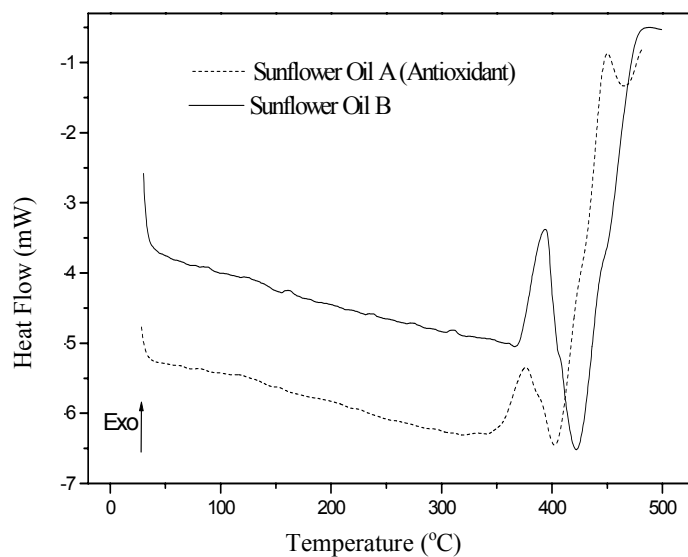


Figure 4: DSC curves for sunflower oils with and without artificial antioxidants.

Table 2: Polymerization and decomposition enthalpies (J.g^{-1}) of sunflower oils.

Sunflower oils	Heating rate ($^{\circ}\text{Cmin}^{-1}$)	ΔH_{pol}	$-\Delta H_{\text{dec}}$
A	5	11.30	32.84
	10	7.93	28.93
	20	1.74	26.90
B	5	18.76	55.26
	10	8.13	42.50
	20	2.61	18.13

Heat Capacity

The standard molar heat capacities in the liquid phase were determined by the method described earlier. The curves related to the standard heat capacities in the liquid phase of sunflower oils are shown in Fig. 5.

The specific heat values for the sunflower oils analyzed do not vary substantially. The calculated C_p values are in agreement with those found in the literature for other vegetable oils (Kasprzycka-Guttman et al., 1995).

Kinetic Parameters

Kinetic parameters for the three steps of thermal decomposition of sunflower oils were determined by using an interval of decomposed fraction (α) of 0.10 to 0.90 and applying the thermogravimetric data in the Program for Determination of Kinetic Parameters developed in Turbo Basic language.

The program for determination of kinetic parameters calculates the reaction order (n), activation energy (E_a) and frequency factor (A) by the approximation and integral methods, using kinetic equations proposed by Coats and Redfern (CR), Horowitz and Meltzger (HM), Madhusudanan (MD) and Van Krevelen (VK) (Coats and Redfern, 1964; Horowitz and Meltzger, 1963; Madhusudanan et al., 1993; Van Krevelen et al., 1951). The calculated kinetic parameters and linear correlation

coefficient (r) found for all the steps in thermal decomposition of sunflower oils are summarized in Tables 3 and 4.

The different heating rates used resulted the same mechanism, only varying the values of the kinetic parameters. Nevertheless, there was a good correlation between the kinetic parameters obtained by the integration and approximation methods, but the values obtained by the approximation methods were higher than the values obtained by the integration methods, which can be ascribed to the different mathematical treatments of the methods.

The results presented in Tables 3 and 4 indicate that the first step in the thermal decomposition of sunflower oils corresponds to the first-order reaction, whereas, the second and the third steps behave as second-order reactions.

The medium activation energy from sunflower oil with artificial antioxidants was higher than that from sunflower oil without artificial antioxidants, indicating that the artificial antioxidant citric acid produced an increase in thermal stability of the oils analyzed.

The increase in activation energy in relation to the steps in thermal decomposition of samples occurred due to the possible break in the molecular bonds of unsaturated fatty acid, which than the molecular bonds of is are less stable saturated fatty acids, requiring higher activation energy for degradation.

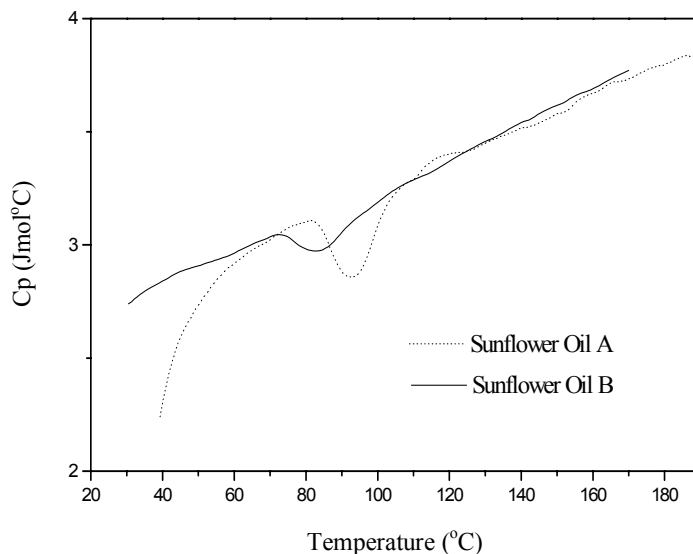


Figure 5: C_p curves for sunflower oils.

Table 3: Kinetic parameters obtained by thermogravimetry for the steps in thermal decomposition of sunflower oil A.

Kinetic method	Kinetic parameters	Steps		
		1	2	3
CR	n	0.94	2.11	2.07
	E_a [kJmol ⁻¹]	92.76	288.39	355.95
	A [s ⁻¹]	1.7E+04	1.5E+19	2.9E+21
	r	1.0000	0.9994	0.9991
MD	n	0.92	2.12	2.11
	E_a [kJmol ⁻¹]	92.45	289.48	352.14
	A [s ⁻¹]	1.8E+04	1.7E+19	1.5E+22
	r	1.0000	0.9994	0.9990
HM	n	1.06	2.13	2.15
	E_a [kJmol ⁻¹]	107.16	299.45	382.19
	A [s ⁻¹]	2.4E+06	9.9E+20	3.2E+23
	r	0.9999	0.9993	0.9994
VK	n	0.94	2.06	2.10
	E_a [kJmol ⁻¹]	94.48	298.37	398.96
	A [s ⁻¹]	7.7E+10	4.4E+23	3.3E+28
	r	1.0000	0.9980	1.0000

Table 4: Kinetic parameters obtained by thermogravimetry for the steps in thermal decomposition of sunflower oil B

Kinetic method	Kinetic parameters	Steps		
		1	2	3
CR	n	0.96	2.08	1.98
	E_a [kJmol ⁻¹]	86.88	208.81	307.43
	A [s ⁻¹]	1.7E+07	2.7E+13	4.5E+17
	r	0.9998	0.9990	0.9992
MD	n	0.95	2.03	1.88
	E_a [kJmol ⁻¹]	87.61	205.28	296.88
	A [s ⁻¹]	1.7E+07	1.5E+13	8.9E+16
	r	0.9998	0.9990	0.9991
HM	n	0.99	2.12	2.05
	E_a [kJmol ⁻¹]	108.93	215.67	327.73
	A [s ⁻¹]	8.5E+09	2.7E+14	1.0E+19
	r	0.9995	0.9960	0.9991
VK	n	0.97	2.06	1.96
	E_a [kJmol ⁻¹]	90.28	208.88	311.74
	A [s ⁻¹]	1.0E+14	1.2E+18	5.4E+23
	r	0.9948	1.0000	0.9993

Thermal Degradation

The study of oils before their use in food permits data to be obtained on the influence of variables (time, temperature) on their thermal decomposition. Comparison with data obtained in earlier tests increases the amount of data available, thereby allowing better conclusions to be drawn in this study.

To verify the dependence of the thermogravimetric profiles for the commercial edible oils on frying time and temperature, the oils were heated to 190°C and the TG curves were obtained after 0.5, 4.0 and 8.0 h of heating and are shown in Fig. 6.

According to the thermogravimetric curves for sunflower oil with and without antioxidants as a function of frying time, it can be verified that the

onset temperature of thermal decomposition of the oils analyzed decreased with the increase in frying time, i.e., an increase in frying time led to an increase in the degradation of these oils. This is caused by the decrease in unsaturation due to prior heat treatment, resulting in degradation of the samples of edible oil under analysis.

The auto-oxidation of unsaturated fatty acids produces a decrease in the thermal stability of the vegetable oils, causing a decrease in the oxidative induction time. Factors such as change in color, increase in viscosity and unpleasant odor are observed in the process of degradation of these oils.

The data obtained from TG/DTG curves for the process of degradation of sunflower oils are summarized in Table 5.

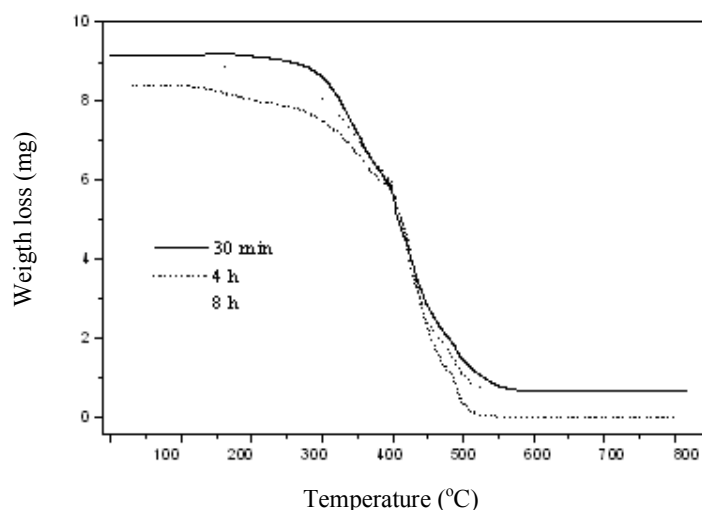


Figure 6: TG curves for sunflower oil A under frying conditions.

Table 5: Decomposition onset temperature (T_{onset}) of sunflower oils after different frying times.

Time (h)	T_{onset} (°C)	
	Sunflower Oil A	Sunflower Oil B
0	246.67	218.78
0.5	192.80	207.78
4	186.51	177.95
8	184.66	169.60

During the heating of the vegetable oils in the process of frying, a complex series of reactions produces numerous degradation compounds. With the occurrence of the thermal reactions, the functional, sensorial and nutritional qualities are modified. The oils repeatedly used in frying without

immersion undergo degradation by oxidative reactions. In this case, as shown in Table 5, the loss of stability is accelerated by the increase in process time, which is responsible for changes in the physicochemical and organoleptic characteristics of the sunflower oils.

During prolonged heating, edible vegetable oils, including sunflower oils with and without artificial antioxidants, undergo the process of thermal degradation resulting in oxidative rancidity, resulting in the formation of hydroperoxides and other products of degradation that can liberate volatile compounds such as hydrocarbons, aldehydes, ketones, furans and carboxylic acids, lower the temperature of onset of thermal decomposition (T_{onset}) of the samples analyzed.

CONCLUSIONS

Thermoanalytic and kinetic properties of sunflower oils are dependent on the composition of fatty acids and are influenced by artificial antioxidants.

The thermoanalytic methods were considered to be versatile techniques for this work, because in addition to the study of thermal stability and of the deterioration occurring in frying, they require only a small sample mass, making it possible to obtain results more rapidly and enabling verification of presence of the artificial antioxidants.

ACKNOWLEDGEMENT

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

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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.

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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 $EO_t = \{(IN_0/2A_j)/[100 + (IN_0/2A_j) \cdot A_0]\} \cdot A_0 \cdot 100$, where $A_j = 126.9045$ 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.

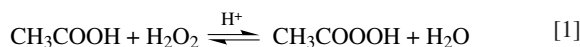
Using two strong ion exchange resins of the sulfonated polystyrene type, Amberlite IR-120 and Dowex 50X, for the epoxidation of soybean oil in bulk produced no significant difference in the maximal epoxy oxygen content (syntheses S8 and S11).

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-

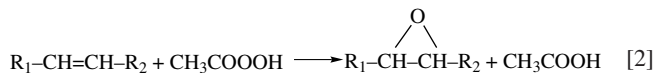
tion rate, conversion of double bonds (X), relative epoxy yield (RYE), and SE were found to increase with increasing temperature. At the highest temperature, the shortest reaction time (t) was obtained, and the maximal EO content of 5.99% was reached. Since the same relative epoxy yield but somewhat 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.

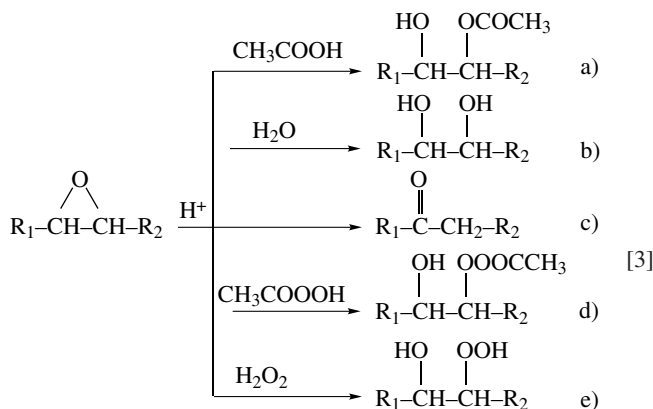
Model selection. *In situ* epoxidation of soybean oil with peracetic acid in the presence of an ion exchange resin is a heterogeneous catalytic process in which peracetic acid formation is an acid-catalyzed reaction:



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

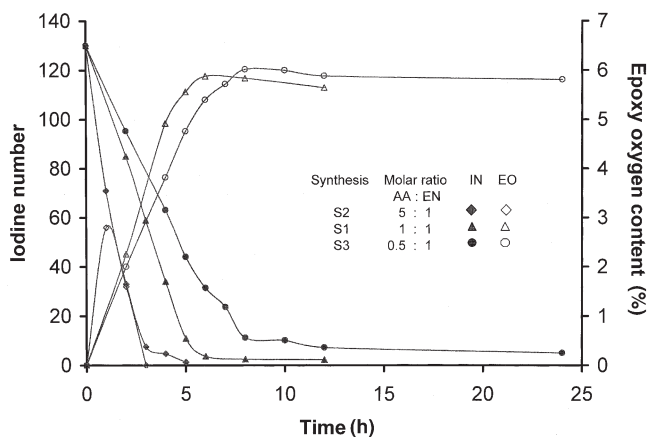


FIG. 1. Effect of different molar ratios of acetic acid (AA) to ethylenic unsaturation (EN) of oil on the *in situ* epoxidation of soybean oil in benzene (20 wt%) with 1.1 moles of 30% hydrogen peroxide at 75°C, and in the presence of 5% of Amberlite IR 120 (Rohm & Hass Co., Philadelphia, PA). IN , iodine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

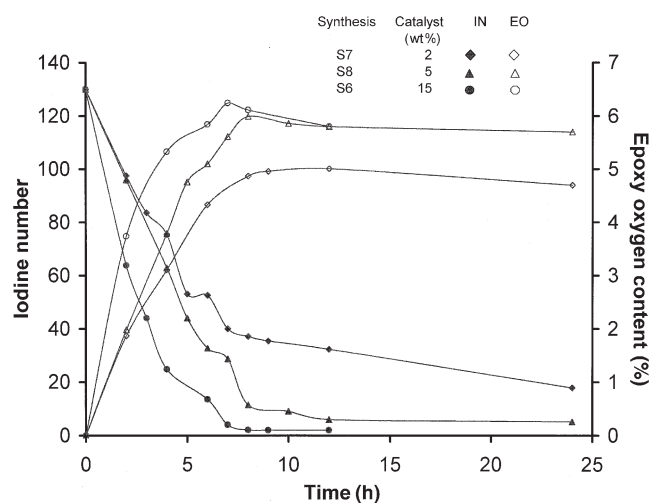


FIG. 2. Effect of the amount of catalyst on *in situ* epoxidation of soybean oil in bulk at 75°C, with molar ratio of ethylenic unsaturation of oil/acetic acid/hydrogen peroxide (30%) = 1:0.5:1.1. For abbreviations see Figure 1.

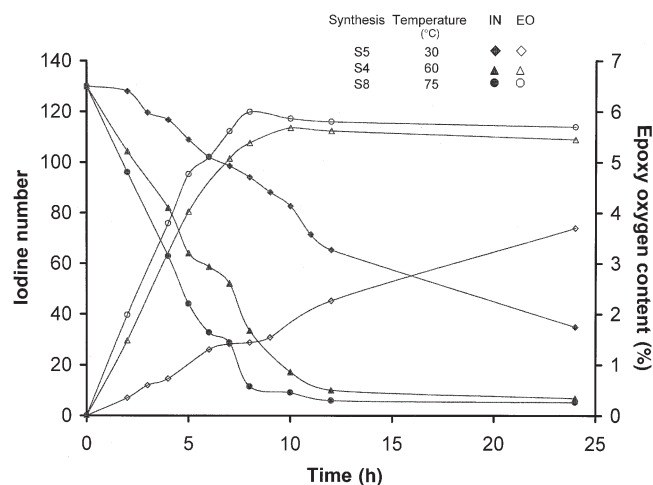


FIG. 3. Influence of temperature on *in situ* epoxidation of soybean oil in bulk with 1.1 moles of hydrogen peroxide (30%) and 0.5 mole of acetic acid in the presence of 5% of Amberlite IR 120. For abbreviations and company source, see Figure 1.

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

Model no.	Reaction ^b taken into consideration				Chemisorption					
					Adsorption				Determining step	
	Homogeneous	Order	Heterogeneous	Order	Without	With	Reversible	Irreversible		
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	—	All steps	—	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-

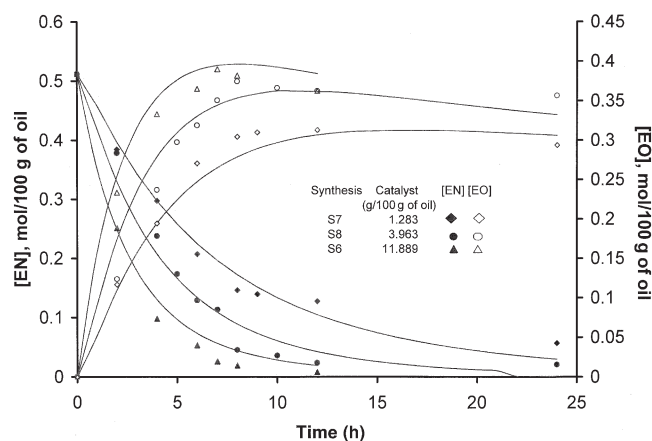
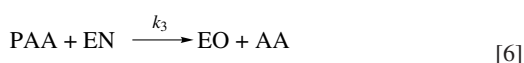
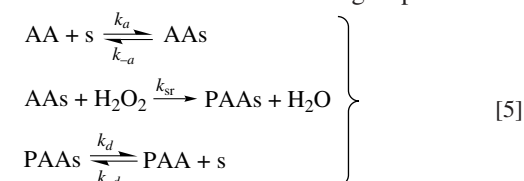


FIG. 4. Time dependence of experimentally determined (points) and calculated (solid curves) concentrations of ethylenic unsaturation of oil [EN] and epoxy oxygen [EO] for the *in situ* epoxidation of soybean oil in bulk at 75°C, with 1.1 moles of hydrogen peroxide (30%) and 0.5 mole of acetic acid, in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